

KINETICS AND MECHANISMS OF PYROLYSIS OF POLYBOROSILAZANES TO
THERMALLY STABLE AMORPHOUS AND CRYSTALLINE STATES
BY A NOVEL SYNTHESIS ROUTE

By
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‘Surely goodness and love will follow me all the days of my life, and I will dwell in the house of the LORD forever’
- Psalm 23:6

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A new type of SiBCN ceramic is being investigated and considered for a variety of high temperature applications. SiBCN ceramics have been produced by various synthesis methods in different monomer systems and subsequent pyrolysis processes at different temperatures. The final ceramic composition and structure are significantly affected by the selection of the polymer precursor material and the pyrolysis conditions. Although detailed studies or discussions of the synthesis of the preceramic materials are rather limited, considerable progress has been achieved by alternative synthesis approaches in recent decades.

Our study introduced a novel synthesis route to produce thermally stable SiBCN-based ceramics. This route also is approximately an order of magnitude less costly, and processing is simpler and faster than other routes investigated to date. Polyborosilazane was synthesized by using three monomers. Polymerization is initiated

by substituting chlorines attached to silicon and boron for trimethylsilylamino groups in hexamethyldisilazane (HMDZ). The polyborosilazane becomes an amorphous structure with crosslinked bonds during the elimination of $[(CH_3)_3SiCl]_n$. In a second stage, an intermolecular condensation reaction occurred, with the loss of HMDZ in the absence of crosslinking agents. This new route allows the SiBCN preceramic polymers to be produced with a high yield, and without a special filtering step.

The polyborosilazane preceramic polymers were modified by altering the monomers and their respective molar ratios, and by optimizing the reaction temperature during polymerization. Remarkably, the pyrolyzed ceramic products remain amorphous to temperatures up to 1600 °C. Results show that SiBCN-containing ceramics have enough thermal stability to retard crystallization.

The chemical structure and composition of the polyborosilazane preceramic polymers were postulated and analyzed via a combination of structural and compositional analysis. By pyrolysis of the preceramic polymers, the mechanisms and kinetics of the structural and compositional changes associated with thermal decomposition were determined.

Hydrothermal stability of the pyrolyzed or partially pyrolyzed products was evaluated by exposing material to 350 °C and 3000 psi in water. After hydrothermal exposures, the boron content of the effluent from a dissolved polyborosilazane preceramic polymer in water was determined to be below 200 ppm. Results show that the low-cost polyborosilazane preceramic polymer remains hydrothermally stable, under both severe hydrothermal conditions and elevated temperature heat treatments.

CHAPTER 1 INTRODUCTION

Non-oxide ceramics such as silicon carbide (SiC), silicon nitride (Si_3N_4), boron nitride (BN), and boron carbide (B_4C) offer excellent performance for thermomechanical applications because they have high stiffness and especially structural stability under environmental extremes. Several research groups over the past 30 years focused on the preparation of SiC, Si_3N_4 or SiCN-based materials from organosilicon materials.

The synthesis of binary component ceramics such as SiC and Si_3N_4 that can be obtained by pyrolysis (or thermolysis) from polysilanes¹ and polycarbosilanes² (SiC) or polysilazanes (Si_3N_4),³ as well as the ternary silicon carbonitride (SiCN) ceramics which are synthesized from carbon-containing polysilazanes,⁴ has been moderately investigated since the mid 1970s. Advantages of the synthesis of such non-oxide ceramics by polymer pyrolysis, as compared with conventional methods such as melting or sintering, are high chemical purity, microstructural homogeneity, low processing temperatures, and versatile fabrication potentials.⁵ In addition, unique amorphous structures can be obtained through pyrolysis route.

Currently all of the aforementioned binary ceramics are in use as structural ceramics, fiber-reinforced composites, and so on. During the past decades, the use of multi-component system materials has been extended by various synthesis processes, and substantial improvements with respect to the high temperature properties over simple binary materials have been obtained. Multi-component materials are typically fabricated via conventional solid state reactions, including mixing, milling, and sintering of binary

carbide/nitride powders such as SiC, Si₃N₄, BN, and B₄C. However, there are a variety of technical challenges associated with fabricating these complex materials. For example, the decomposition temperatures of the reactants are very different. Ceramic powder processing introduces undesirable contamination and inhomogeneities from the milling media, which can induce phase separation and decomposition of ceramic material into its binary border phases, and reduce the service temperature of the product. Inter-diffusion of the covalent carbides and nitrides proceeds extremely slowly. Thus, solid-state syntheses of multinary compounds from the binary border phases require the use of sintering additives or acceptance of appreciable porosity.

Preceramic polymer precursors possess the potential to remove these processing disadvantages as well as to obtain novel ceramic materials. Final ceramic products can be obtained from the synthesis of single source precursor. To attain a final ceramic structure, the polymeric precursors are transformed into ceramic materials by subsequent pyrolyses, which are generally performed in an inert gas atmosphere. Specifically, the transformation of such precursors into the corresponding ceramics has been achieved by solid-state pyrolysis or by the deposition of the molecular units via the vapor (CVD, Chemical Vapor Deposition) or liquid (CLD, Chemical Liquid Deposition) state.

The possibility to vary the structure and composition of the polymers allows one to tailor the properties of the ceramic. Further, in contrast to materials derived from Si-C-N ternary precursors, which are limited by vaporization, the incorporation of boron can lead to ceramics with outstanding high temperature oxidation resistance and thermal stability.⁶ The reasons for this remarkable characteristic are not yet understood. In several recent publications, it has been shown that boron retards the crystallization behavior and the

weight loss during thermal treatment experiments. Existence of the crystalline region in the structure plays a key role as origin that can stimulate the fracture of material.

Precursor derived ceramics may have a tendency to show better high temperature properties, e.g., crystallization onset temperatures, going from binary through secondary to ternary phases. In particular, SiBCN-based ceramics have shown a number of advantages compared to the SiCN system, including higher thermal stability and oxidation resistance, as well as higher crystallization temperatures and ceramic yields. SiBCN-based ceramics have been utilized for high temperature applications with the same range of primary properties as for SiC and Si_3N_4 . Since their performance depends strongly on how the precursors are synthesized, novel synthesis technology combines the polymer precursor process for high-temperature SiBCN ceramics to yield highly complex crosslinked amorphous ceramic microstructures.

The primary focus of our research is summarized as follows. First, specific attention is devoted to developing novel and innovative synthesis technique for SiBCN-based preceramic polymers that can be utilized in high temperature and hydrothermal environments. A new type of the preceramic polymer using a novel synthesis route is introduced. This synthesis process is far less expensive, simpler and faster than other routes discovered to date. In addition, the obtained preceramic polymer from this synthesis route maintains multinary and amorphous ceramic structure to assure thermal and mechanical stability even at much higher temperature.

Second, the obtained preceramic polymers are identified by various characterization techniques. The proposed possible structure of the preceramic polymer is characterized by infrared spectroscopy (IR) and magic angle spinning nuclear magnetic

resonance (MAS-NMR). The individual elements in a multi-component system of the preceramic polymer are assessed using atomic absorption spectroscopy (AA) and elemental analysis (EA). Existence of byproducts in the composition of the preceramic polymer is investigated quantitatively or qualitatively by IR, energy dispersive spectroscopy (EDS) and bomb method (ASTM D808). The results assist in determining the composition evolution occurred in the preceramic polymer (precursor) after polymerization. Another method to investigate thermal behavior is the use of thermal analysis such as thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Third, the pyrolysis is executed in a horizontal tube furnace up to 1600 °C under inert atmosphere. Through this process, the preceramic polymers are converted into a final ceramic structure whether it consists of an amorphous structure or a crystalline at high temperatures. Subsequently, the final structure of the preceramic polymers can be determined by x-ray diffraction spectroscopy (XRD). The structural and compositional changes after an elevated temperature exposure are able to be identified by IR and EA. Such studies are especially able to demonstrate the main structure of polyborosilazane and the pyrolysis reaction mechanism at different temperatures. The results can reveal a short-range order of the elements that can be formed during pyrolysis together with the data obtained from compositional analysis.

Fourth, after characterization of a new type of preceramic polymer, such reaction variables as the molar ratio and reaction temperature are changed to verify these influences. The starting materials are modified by varying with the size of the pendant group attached to the silicon site that leads to a change of the reactivity and the final

structure of precursor during polymerization. This change eventually enables the precursor to affect the thermal behavior at high temperatures.

Lastly, the applicable research reveals that the preceramic polymer materials are suitable for integration into nuclear power generation devices. Our research step leads to a novel manufacturing process of preceramic polymer with advanced thermal and hydraulic properties. Application of the preceramic polymer to nuclear environments is investigated by using an autoclave test in a condition similar to nuclear reactor assembly. Examination of PCP specimen is performed via inductively coupled plasma (ICP) analysis for the compositional change after autoclave test. The autoclave test for the preceramic polymer contributes to the proposed research in the study of PCP operating in various temperature and environmental conditions. The possibility of the substitution for boron carbide (B_4C) currently used in pressurized water reactor as a filler of alumina (Al_2O_3) matrix is verified.

CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

2.1 Background Information

Researchers have recently discovered thermally stable SiBCN-based ceramics. These amorphous non-oxide ceramics can be obtained from a single source precursor polymer. Precursor polymers for silicon nitride-, silicon carbide-, and boron nitride-based SiBCN ceramics have been derived from a variety of organometallic polymer compounds. Their excellent thermal stability and resistance to oxidation at a very high temperature have been studied in the recent decade. With their potential high strength and good toughness, as well as their thermal shock, corrosion, and creep resistance, high temperature miniature devices, and monolithic engineering devices provide a unique combination of properties for high-temperature applications.⁷ In addition, these polymers may serve as functional tools in Burnable Poison Rod Assemblies (BPRAs) and Spent Fuel Containers (SFC) due to their potentially high hydrothermal resistance and ability to retain both hydrogen and boron.⁸

Several advantages of preceramic polymers include; the ability to prepare ceramic forms which are difficult to obtain from conventional powder processing methods (e.g., fibers, films, foams), the ability to lower the processing temperatures than those of conventional technologies, and the ability to prepare ceramics with high and controlled purity. An idealized preceramic polymer shows a compromise of the following properties, which are sometimes incompatible. First, a molecular weight is sufficiently high to prevent volatilization of oligomers. For example, weight loss and gas evolution is

as low as possible during pyrolysis to limit shrinkage in most applications. Second, a preceramic polymer exists in a polymeric structure with cages or rings to decrease the elimination of volatile fragments resulting from backbone cleavage. Third, viscoelastic properties (fusibility, malleability, or solubility) are required to apply the polymer in the desired shape before the pyrolysis process. Fourth, latent reactivity (functional substituents) to obtain thermosetting or curing properties are present in a preceramic polymer. Fifth, a preceramic polymer should contain low organic groups, which can increase ceramic yield and avoid the production of undesirable free excess carbon. Obviously, different constituents will strongly affect the final ceramic compositions. One of the main challenges in the preceramic polymer strategy is to design the desirable structures under the condition in which splitting of the main backbone, due to chain cleavage followed by backbiting and evolution of volatile products, is prevented.

It has been recognized that the various substituents (e.g., hydrogen and any other pendent group) play a crucial role on the polymer properties, its thermal behavior, and the pyrolysis mechanisms. Thus, some studies deal with these questions, and general patterns of behavior have been noted. However, detailed mechanisms have not been clearly clarified. Unlike low-pressure thermochemistry of organosilicon compounds which is relatively well-documented,^{9,10} much less is known about the high-temperature behavior of organosilicon compounds in the liquid and solid condensed phases as well as the reaction mechanisms at the gas-liquid (or gas-solid) interface.

There are several major categories of the ceramics which are built up by novel materials from molecular units in order to design the material on an atomic scale.^{7,11} According to a recently progressive process, preceramic polymers are synthesized from

monomer units. After crosslinking of such precursors, the obtained preceramic networks are transformed into amorphous materials by pyrolysis. Further increase of the temperature yields thermodynamically metastable and/or stable crystalline phases.

Figure 2-1 shows the schematic steps for making a final ceramic material.¹² The ceramization of preceramic polymers derived from precursor syntheses can be classified by three chemical approaches. First, pyrolysis of a liquid or soluble polymeric precursor coincides with synthesis. Second, pyrolysis is performed on two or more solid processible polymeric precursors which are prepared by a different synthesis method. And third, by using a single source preceramic polymer, the final ceramic is obtained after pyrolysis.¹³

Due to the lack of appropriate monomers and polymers, few successes have been realized with the single source approach. Attempts to obtain bulk ceramics by pyrolysis of liquid or crosslinked polysilazane powders were not satisfactory due to the evolution of low molecules during pyrolysis, which resulted in extensive pores or cracks of the pyrolyzed products. In recent years, many research groups have reported and developed a single source approach with various synthesis routes to improve the properties of polymer precursors and reduce the disadvantages. The use of different monomer units affects the ceramic yield, the chemical composition, and the microstructure of precursor-derived ceramics. Figure 2-2 shows examples of the polymers that have been synthesized from monomers for the preparation of silicon carbide and silicon nitride-based ceramics.

The study of polymer derived ceramics from polysilazanes was first started by Verbeek¹⁴ who synthesized N-methyl polysilazane by reacting trichloromethylsilane with methylamine. Table 2-1 shows chronological list of some polysilazanes and

polyborosilazane used for producing Si(B)CN ($\text{Si}_3\text{N}_4\text{-SiC}$) ceramics.¹⁵ Such multinary ceramics and composite materials have been of interest due to their enhanced properties.

For example, as a conventional method, the addition of boron nitride leads to better thermal shock resistance in hot-pressed silicon nitride ceramics. Thermogravimetric analysis and oxidation studies have revealed that for reasons that are not understood, ceramics containing boron give the improved protection from decomposition. Figure 2-3 shows the comparison with binary, ternary and quaternary system obtained from polymer precursor synthesis for the thermal behavior.¹⁶ As described before, the presence of boron in the composition of preceramic polymer or final ceramic reduces atomic mobility and retards phase transformation. It is likely that BN bonds act as diffusion barriers that inhibit grain growth of SiC and Si_3N_4 crystals after crystallization. However, a plausible mechanism or explanation as to why boron atoms have this effect has not yet been put forward.

One of the more noticeable disadvantages of non-oxide ceramics compared to oxide ceramics is their low resistance toward oxidative attack.¹² Since all preceramic polymers for SiBCN ceramics are extremely sensitive to oxygen and moisture, they have to be handled under strictly inert conditions during pyrolysis. For the stage of pyrolysis, oxygen contamination may occur with up to 10% oxygen content. Oxygen impurities exceeding 1 wt% significantly affect the performance of the ceramic product if they are not burned off during sintering. Thus, this issue is of crucial importance. In contrast to pure silicon carbide and silicon nitride for the susceptibility of oxygen, SiBCN ceramics represent the high resistance to oxidation. Figure 2-4 shows the significant weight loss of silicon carbide and silicon nitride, which oxidized at 1000 °C and 1130 °C. Even at 1700 °C,

there is no mass change detectable in the case of the SiBCN ceramics obtained from monomer route, whereas there is a slight weight increase in the case of the SiBCN ceramics obtained from polymer route.¹⁷ This suggests either that active and passive oxidation occur simultaneously or that a thin and dense oxide layer forms, protecting the ceramic samples from further oxidation.

For a better thermal stability and oxidation resistance of a ceramic product, its development can be traced back to the origin, that is, polymeric precursor which is chemically and structurally stable. Molecular compounds of silicon and boron that can be employed as molecular precursors for processing non-oxide ceramics along the polymer route have to fulfill a number of conditions. First of all, they must bear functionalities that allow them to be polymerized by any of the processes established in chemistry, and they have to contain nitrogen and/or carbon. At least, they should offer the opportunity for inserting nitrogen and carbon during polymerization. Moreover, as developments in the field of large scale applications, monomer or polymer precursors should be easily available and inexpensive.

General formulae for molecular entities consist of silicon and boron functionalities. The functional groups of silicon can be exclusively halide, amide, hydride, or smart leaving groups like trimethylsilyl (TMS) or trimethylstannyl, or combinations of them. A fraction, but never all, of the sites attached to silicon may be occupied by saturated or unsaturated organic groups. In the case of boron hydrides, the Lewis base adducts are preferred because they are much easier to handle during processing than the pure boranes. The halide, amide, hydride, unsaturated hydrocarbon, trimethylsilyl, and stannyl functions can be employed for different kinds of polymerization reactions, while alkyl

and aryl groups block the site where they are present for any process. Thus, by adjusting the number of hydrocarbon ligands, methyl being used selectively, the degree of crosslinking and, consequently, the rheological properties of the polymer can be modified. In general, halides and alkyl-halides of silicon, boron, phosphorus, and aluminum are commercially available, which holds true for silicon in particular, since large scale industrial products are based on silicon tetrachloride, silicon alkyl chlorides, or silicon aryl chlorides.

Molecular precursors, containing only one electropositive element, can be used for the production of nitrides, carbides, as well as of carbonitrides. When these precursors are copolymerized, quaternary or ternary ceramics, e.g., within the systems SiBCN, SiBN, or SiBC, are also accessible. However, condensation reaction rates differ considerably depending on starting monomers, their spatial inhomogeneities of the elemental distributions, and use of a catalyst during polymerization. Such inhomogeneities usually induce phase separation and decompositions of the multinary ceramic into its binary border phases.¹⁸ It has been shown that these effects can be resolved by using single source precursors. One and the same molecule contains the different metals or half metals in the ratio desired for the final ceramic, linked via nitrogen and/or carbon. Preferably, the backbone of such a single source precursor should survive the full sequence of processing, and should be present as structural units in the final solid material.

The so-called precursor derived-polysilazane process is a conventional method for preparing SiBCN-based materials. Among these precursors, polyborosilazane has been synthesized according to the monomer route suggested by Riedel and colleagues.^{6,19} The polymeric precursors are prepared via hydroboration of polymethylvinylsilazane using

dichloromethylvinylsilane and BH_3SMe_2 . Potential problems include both the hydrolysis of the product and the elimination of byproducts, such as ammonium chloride.¹²

Dieter et al. reported that the development of the SiBN_3C compound was initiated by the pyrolysis of a preceramic N-methylpolyborosilazane made from the single source precursor $\text{Cl}_3\text{Si-NH-BCl}_2$ (Trichlorosilylamino-dichloroborane; TADB).²⁰ TADB is generated from the reaction of hexamethyldisilazane (HMDZ) with methyltrichlorosilane. The subsequent formation of 1, 1-dichlorotetramethyldisilazane can be reacted even further with boron trichloride. This route allows rapid polymerization by additional ammonolysis (or aminolysis) and polycondensation to produce the final structure.

In the process described by Cannady et al., an R_3SiNH -containing hydrosilazane polymer reacts in an inert and essentially anhydrous atmosphere of trichlorosilane with a disilazane.²¹ Non-oxide ceramic materials derived from the above three routes, such as polyorganoborosilazane, hydridopolysilazane (HPZ) and hydrosilazane, are promising candidates for high temperature applications. The synthesis processes of single source precursors require several steps. Unfortunately, to date processing of the materials has been laborious, complex, hazardous, and very expensive.¹⁵

The three different examples described above substantially give a motivation to establish a new synthesis route with respect to chemical step and use of disilazane monomer and crosslinking agent. In our study, a novel, simple, and potentially inexpensive synthesis method is investigated. The proposed method requires no additional crosslinking reagents for propagating the chemical reaction of the preceramic polymer with a final SiBCN -based structure. In addition, the pyrolyzed polymer remains amorphous, stable and oxidation-resistant at relatively high temperatures. Therefore, the

precursors have potential application in processing of ceramic fibers, coatings, composites, and nuclear assemblies.

The alumina matrix (Al_2O_3) of boron carbide (B_4C) is currently used in pressurized water reactor (PWR) as the burnable poison matrix material in the burnable poison rod assemblies. However, there are some problems. The displacement of the moderating coolant in the guide tubes whose volume they occupy presents a costly penalty at the end of each cycle. A novel SiBCN polymeric burnable poison material containing a hydrogen atom will burn out and absorb neutrons effectively at the beginning of cycle where needed. This polymeric material will reduce the water displacement penalty caused by the burnable poison rod assemblies, which displaces the water moderator in the control rod guide tubes. The much higher hydrogen content of the SiBCN polymer actually reduces the moderator displacement reactivity penalty and results in a longer cycle lifetime. It is estimated that a SiBCN moderator polymer could generate a cost saving of approximately six million dollars for a 24-month cycle of a nuclear reactor.

2.2 Literature Review

This literature review describes SiC, Si_3N_4 , SiCN and SiBCN ceramics which are obtained from both the synthesis and the pyrolysis of polysilanes, polycarbosilanes, and polysilazanes.⁵ Since the type of the backbone and the functional side chains of precursor molecules substantially influence the ceramic yield, chemical composition, and microstructure of precursor-derived ceramics, a variety of different compounds has been investigated as starting materials. Some examples which have been synthesized from monomers for the preparation of SiC, Si_3N_4 and SiCN-based ceramics are briefly described. As one of the precursors for SiBCN-based ceramics, boron-containing polycarbosilanes,^{22,23} carbon-containing polyborosilazanes,^{24,25} and silylated borazine

derivatives^{26,27} have been shown to be excellent precursor materials in the quaternary system. Their synthesis routes and properties have been reviewed in detail.

2.2.1 Polymers as Precursors for Ceramics

SiC precursors are most often synthesized using polysilanes (PSs) which are further converted into polycarbosilanes (PCSs) upon pyrolysis. After the pioneering work of Verbeek²⁸ and of Yajima²⁹ whose strategy has allowed the production of industrial SiC-based fibers (Nicalon and Tyranno), a number of reports have described the preparation of PSs,^{30,31} PCSs³² and SiC-based materials upon pyrolysis of the PCSs, after their eventual spinning and curing. PCSs were also prepared by more direct approaches, avoiding PS intermediates.³³

With respect to SiCN- or Si₃N₄-based materials, the potential of polysilazanes (PSZs) for making silicon nitride or carbonitride³⁴⁻³⁶ were recognized in the 1970s, but the first intensive investigations focused on the preparation of inorganic materials came from Verbeek.³⁷ Most routes to such ceramics involve PSZs as the basic preceramic polymer precursors.^{38,39} However, some synthesis approaches produce polycarbosilazanes (PCSZs) as a precursor of silicon carbonitride.

2.2.1.1 SiC precursors

For SiC precursors, the direct routes to PCSs were proposed. The use of PSs for directly making silicon carbide materials (e.g., without the pyrolysis step that affords PCSs) had received special attention. The Yajima routes constitute basic references from both fundamental and industrial points of view. Concerning PCSs themselves, a number of reports mention their preparation by methods different from the pyrolysis of polysilanes, since the first report by Rochow in 1949 and the further preparation of oligomers, important results concerning the synthesis of high polymers containing the

$-(R_2SiCH_2)_n-$ sequence were reported.^{40,41} Yajima's work is based on the transformations of SiC material from PCS. However, pyrolysis is necessary because the PCS is not directly obtained from the synthesis of PS. The major drawbacks of this method are the cost of dodecamethylcyclotrihexasilane and the use of an autoclave at 400 °C under argon.⁴²

Later, Yajima proposed a simpler and more economical synthesis of a PCS⁴³ by heating polydimethylsilane (PDMS) obtained from Me_2SiCl_2 and Na in xylene at atmospheric pressure under argon up to 470 °C. However, SiC fibers could be obtained upon pyrolysis under vacuum after air curing.⁴⁴ Finally, the commercially available PCS was synthesized by heating PDMS under pressure. The PCSs were not found to possess comparable mechanical properties.⁴⁵ Adding small amounts of $(Ph_2Si)_n$ in PDMS or Ph_2SiCl_2 in Me_2SiCl_2 and subsequent pyrolysis resulted in PCS.^{46,47} The product gave a better spinnability than the former PCS, which made a commercial SiC fiber. However, these modifications remained in the use of an autoclave. To avoid the use of an autoclave, alternative PCS precursors were obtained from PDMS at 350 °C under atmospheric pressure, with the use of an initiator or catalyst polyborodiphenylsiloxane (PBDPSO).⁴⁸ The PBDPSO was used to transform PSs containing methyl and phenyl groups into boron-containing PCSs.⁴⁹

In 1991, Lipowitz obtained a nearly pure, nanocrystalline SiC fiber with less than 0.1 wt% oxygen by melt-spinning of various precursors, crosslinking, and then heating at 1600 °C, while a dense structure and high tensile strength were preserved by using a nonspecified additive.⁵⁰ Polycrystalline silicon carbide-based fibers were prepared by treatment of the precursors with B_2H_6 , BCl_3 , or boron vapor.^{51,52} Especially, polycrystalline SiC fibers with improved thermal stability were obtained. In addition,

curing Yajima PCSs by γ -ray or electron irradiation followed by heat treatment at 1200 °C to 2000 °C resulted in a high Nicalon SiC fiber with 0.4 wt% oxygen and improved thermal properties.

Among the numerous reports in this field, Baney et al. developed a new class of polysilazane prepared from the tetrabutylphosphonium chloride catalyzed Si-Si/Si-C bond redistribution of methylchlorodisilanes, which showed a polycyclic structure with approximately seven rings per molecule.⁵³ Derivatives of the parent polymethylchlorodisilane polymer were prepared by modifying the residual silicon-chloride bonds. These reactions include alkylation, arylation, amination, reduction, and alcoholysis. In addition, by altering the location of the methyl groups, ring location, as well as size and stereochemistry, other conceivable or thermodynamically stable structures were obtained.⁵⁴

The work from Schilling involving, for instance, vinylchlorosilanes is related to the participation of the vinyl group, which allows the formation of polysilacarbosilanes. He introduced the important concept of branching which defines the ability of a precursor to afford a high ceramic yield. The participation of vinyl groups produced a partial branching, but crosslinking was achieved upon thermal hydrosilylation. Harrod introduced the polysilane synthesis by the dehydrocondensation of polyhydrogenosilanes. The polydehydrocondensation followed a common route to PSs. Among the possible entries to SiC-based materials involving this route, the approach of Harrod and Laine et al. from $-(\text{MeSiH})_n-$ prepared by dehydrocondensation of MeSiH_3 and that of Corriu from $-\text{[HSi(CH}_2\text{CH}_2\text{SiMeH}_2\text{)]}_n-$ should be pointed out because they constitute attractive alternatives.⁵⁵

As a consequence of the Yajima work, a large number of attempts to synthesize effective silicon carbide ceramic precursors were made, especially for fibrous materials, from sources other than PDMS. Several routes were used to obtain such polymers, including PCS from ring-opening polymerization reactions by Smith in 1986,⁵⁶ polycondensation of chloromethylchlorosilanes by Whitmarsh and Interrante in 1991,⁵⁷ copolymerization of 1, 3-disilapentanes by Pillot in 1987,⁵⁸ polycondensation of chlorosilanes with methylene halides by Satori et al. in 1991,⁵⁹ polycondensation of chlorosilanes with acetylides by Barton in 1990,⁶⁰ hydrosilylation reactions by Corriu et al. in 1989,⁶¹ polycondensation of chlorosilanes with unsaturated hydrocarbons by Schilling in 1986,⁶² and dehydropolycondensation of hydrogenosilanes by Harrod et al. in 1985.⁶³ Even though the approaches to the synthesis of PCS are very extensive, these considerations illustrate the influence of the structure of the precursors on the composition of the resulting silicon carbide ceramics.

2.2.1.2 Silicon nitride (Si_3N_4) and silicon carbonitride (SiCN) precursors

Silicon nitride has been known as a valuable refractory material for over a century. Thus, crystalline Si_3N_4 ceramics produced by direct reaction of nitrogen or ammonia with silicon metal in sintering or hot-pressing forming techniques are noted for their chemical inertness, good strength resistance, and extreme hardness.⁶⁴ Another way to make Si_3N_4 that can produce forms with various shapes is chemical vapor deposition (CVD) process using mixtures of gases, typically SiH_4/NH_3 and $\text{SiCl}_4/\text{NH}_3$, in carriers. The composition of the obtained ceramics depends on the compositional, thermal, and surface variations in the deposition environment. In the last decades, it has become very desirable to directly produce Si_3N_4 ceramics as strong, high modulus, small diameter continuous fibers that

could be used in ceramic matrix composites materials (CMC) offering high oxidation resistance and strength.

A promising approach has emerged by using organosilicon polymers, such as polysilazanes (PSZs), polycarbosilazanes (PCSZs), and various nonvolatile resinous materials obtained from silsesquiazanes. It has been known for many years that the reaction of ammonia with silicon tetrachloride yields a heterogeneous material containing Si, N, and H, leading to pure silicon nitride after pyrolysis.⁶⁵ In 1961, Aylett et al. reported the pyrolysis at 520 °C in vacuo of an oligomeric liquid PSZ, $[(\text{MeNHSiH})\text{-NMe}]_x$, yielding a lustrous, copper-colored solid of approximate composition Si_2NC .³⁴ They anticipated that a whole range of compatible materials may be made by this way, giving silicon nitride and possibly carbonitrides.

In 1963, Andrianov et al. obtained resins via the pyrolysis at 400 to 550 °C of PSZs, and Chantrell and Popper suggested the use of inorganic and organometallic polymers as precursors of SiCN-containing ceramics.³⁶ A few years later, the pioneering works of Verbeek and Yajima concerning the preparation of ceramic fibers has sparked intensive efforts to synthesize polymeric ceramic precursors for use in the fabrication of fibers, coatings, and binders.^{14,48} Thereafter, it was shown that a large variety of organosilicon polymers and, in particular, polymetalloxoorganosiloxanes afforded ceramics upon pyrolysis.⁶⁶

Although PSZs have been known for many years, they received little attention from the perspective of applications until Verbeek renewed interest in their utilization as precursors to SiCN ceramics.⁶⁷ Basically, the Si-N bond is most commonly created by the ammonolysis and aminolysis of halogenosilanes. Due to the fact that this bond is cleaved

under various conditions and that it undergoes disproportionation reactions, a wide range of preparative routes to oligomers and polymers have been investigated. As a beneficial consequence of the preceramic polymer development, novel routes to PSZs have recently been developed. The important main approaches to Si-N bond-containing derivatives and PSZ oligomers include ammonolysis, aminolysis, hydrazinolysis of halosilanes, ring-opening of cyclosilazanes, Si-H/N-H dehydrocondensation, and direct synthesis from amines and silicon.

Mukherjee et al. reported that ammonolysis of tetrachlorosilane produced PSZ precursors of Si_3N_4 .⁶⁸ Silicon tetrachloride and ammonia were known to react under various conditions to give a silicon diimide, SiNH_2 , leading to Si_3N_4 after heating up to 1250°C . Ammonolysis of tetrachlorosilane is more particularly useful in the CVD process, although this reaction has also been used for preparing fibrous Si_3N_4 . However, this route did not appear usable for obtaining fusible or soluble preceramic polymers. Seyferth et al. investigated this reaction in polar solvents.³ So, it was apparent that the product did not possess the ideal structure with $-(\text{H}_2\text{SiNH})-$ units. Due to the high functionality of the reactants allowing $\equiv\text{Si-H}/=\text{N-H}$ dehydrocondensation, the final product formed a three-dimensional network.

The stable complexes obtained from polychlorosilanes and tertiary amines brought out beneficial effects in various polycondensation reactions by Isoda et al.⁶⁹ They succeeded in the preparation of a spinnable precursor by using the complex. The oligomeric structure was formed of rings linked by linear segments. Pyrolysis of crosslinked PCSs, PSs, and PSZs under ammonia or hydrazine constitutes a general route highly pure Si_3N_4 , which has been used for the conversion of both bulk precursors and

oxygen-cured PCS fibers.^{70,71} Sulfur was useful in the crosslinking of PCS fibers. When these fibers were pyrolyzed under ammonia, displacement of sulfur by nitrogen occurred above 450 °C to 500 °C.⁷²

Seyferth and Wiseman performed the aminolysis of dichlorosilane with methylamine in the hope of obtaining non-crosslinked precursor with better processability than those obtained from the ammonolysis of dichlorosilane.⁷⁰ Removal of the cyclotetramer by distillation resulted in the preparation of oligo-N-methylsilazanes. The ceramic obtained upon pyrolysis of this precursor consisted of silicon nitride. The presence of N-Me bonds prevent thermal crosslinking, in spite of their relatively low bond dissociation energy.⁹ This means that Si-H bonds alone are not able to induce the formation of a sufficiently branched backbone under pyrolysis and confirms the fact that N-H bonds are also involved in the degradation mechanisms. Ammonolysis of chlorosilanes leaves a small amounts of ammonium chloride which is difficult to remove. This byproduct is undesirable since it contributes to the introduction of chlorine in the precursors while it acts as a catalysis in the splitting of Si-N bonds.

To overcome this problem, Legrow et al. introduced new starting materials.⁷³ Si-C/Si-N disproportionation involving hexamethyldisilazane (HMDZ), leading mainly to trimethylchlorosilane instead of hydrogen chloride as byproduct, was extended to the synthesis of a wide range of precursors, hydridopolysilazane (HPZ). When trichlorosilane and HMDZ are mixed, an exothermic reaction occurs due to Si-Cl/Si-N bond exchange. As the reaction temperature is raised, both trimethylchlorosilane and ammonium chloride are volatilized, reducing the chlorine content of the product. During polymerization, the bulky trimethylsilyl groups along the silazane chain promote cyclization leading to

cyclotetrasilazanes and cyclopentasilazanes. After their pyrolysis, silicones are simultaneously bonded to carbon, nitrogen, or oxygen to give an amorphous silicon carbonitride ceramic.⁷⁴

2.2.2 Polymers as Precursors for SiBCN-based Ceramics

In the last 10 years, a large number of new single source precursors for SiBCN ceramics with different starting monomers have been developed using various synthesis routes.¹⁵ Single source precursor route is mainly used for preparing polymers in the quaternary SiBCN system and in the SiBN and SiBC systems to a minor scale. For example, the most commonly used and versatile process for synthesizing preceramic polymers starts with combining a solution of the respective single source precursor and a cooled mixture of an excess of methylamine, ammonia, and hexane. This reaction mixture is then allowed to heat up to room temperature.

Crosslinking of the organometallic compounds, usually with methylamine, is yielding polyborosilazanes or polyborocarbosilazanes, depending on the bridging atom between silicon and boron. In the case of methylamine, the hydrochloride is filtered off and hexane is removed from the polymer by vacuum distillation. In most cases, the preceramic polymer obtained is a liquid of moderate viscosity. Through a further heat treatment, the condensation of the preceramic polymer can be continued until the desired viscosity is reached.

The quaternary non-oxide ceramics have been investigated mainly for the purpose of high-temperature industrial application. Thus, with regard to a sustainable and cost-effective production of a given single source precursor on a large scale, the syntheses should not involve costly and time-consuming steps. In particular, metallizations (Grignard reactions, lithiations) must be avoided. However, the convenient and

applicable process is challenging since in current molecular chemistry metal organic intermediates play a key role in running syntheses efficiently and well directed. These approaches are affordable in the laboratory, but not yet on a technical scale. Nevertheless, it can be reasonable to apply these advanced techniques of synthetic molecular chemistry while screening new systems. As long as one of the newly found ceramics exhibits promising properties, the synthesis has to be adaptable to the demands of technical feasibility. In any case, the development of single source precursors suitable for mass production is indispensable to select appropriate starting materials which should be readily available, easy to handle, and as cheap as possible.

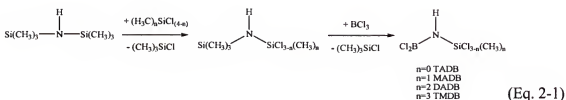
The synthesis of a single source precursor is laborious and even requires several steps. For the formation of element-nitrogen bonds, a large stock of chemical tools developed in basic research can be utilized.⁷⁵ However, the options for establishing element-carbon bonds are limited. Wurtz-analogous dehalogenations play a dominating role, while for more special purposes hydroborations and salt eliminations can be employed. Under some synthesis process condition, carbon from the substituents is inserted into the inorganic network upon pyrolysis. The incorporation of carbon into an SiBN random network system is very crucial in that the thermal durability of the resulting carbonitridic ceramics is attainable, as can be seen from the thermal stability of SiBN compared to SiBN₃C.²⁵

In general, most of the single source precursors have been initiated by monomer with chlorine functionality. To propagate a crosslinked network, the reaction is controlled by two steps, both the constitution of the precursor molecule having an Si-N-B bridge and the crosslinking agent. The recent reviews about the synthesis of some SiCN or

SiBCN materials with crosslinking agents are summarized in Table 2-2.¹⁵ The reaction mechanism for SiBCN preceramic polymers is described more specifically.

Silazane cleavage offers a rather convenient and versatile route to precursors containing a nitrogen bridge between the electropositive elements, e.g., silicon and boron. This approach has been applied during the synthesis of what is arguably the most promising commercial precursor developed to date, (trichlorosilylamino)dichloroborane (TADB). Starting from hexamethyldisilazane (HMDZ), this single source precursor is prepared in a two-step reaction with almost quantitative yields (Equation 2-1).^{25,76}

Trichlorosilylamino-dichloroborane (TADB) was processed using both ammonia and methylamine. Ammonolysis provides an insoluble white solid, while the aminolysis yields N-methylpolyborosilazane (PBS-Me), which is liquid and soluble in hexane. It can be tailored by an appropriate heat treatment to be liquid, meltable, soluble, or unmeltable. For example, heating of the obtained PBS-Me in vacuum at 160 °C for about 2 h gives a meltable and soluble polymeric borosilazane.^{25,76}



Since crosslinking with cyanamide, formamidine, cyanguanidine, guanidine, and melamine in any case leads to insoluble polymers, the respective dimethylamide derivatives instead of fully chlorine functionalized single source precursors have been used during explorative laboratory studies. This requires the additional synthesis step of transforming TADB to $((\text{CH}_3)_2\text{N})_3\text{Si-NH-B}(\text{N}(\text{CH}_3)_2)_2$ (TABB). However, the latter

precursor offers a significant advantage since the byproduct dimethylamine is volatile and can be easily separated from the polymers.^{77,78} TADB and TABB are the single source precursors to which the largest diversity of crosslinking reagents has been applied. In order to reduce the degree of crosslinking during the successive polymerizations, the chlorines attached to silicon have been partly substituted by methyl groups.⁷⁹

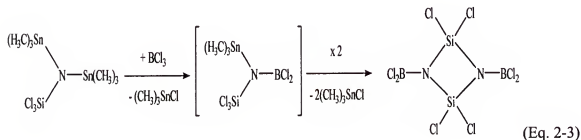
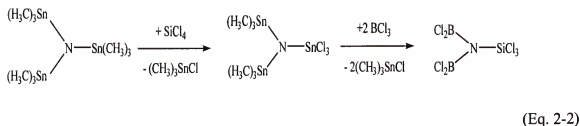
Along the same reaction sequence as shown in Equation 2-1, but using methyl or dimethyl chlorosilane as an educt, (methyldichlorosilylamino) dichloroborane (MADB) and (dimethylchlorosilylamino)dichloroborane (DADB), respectively, were obtained in high yields. The single source precursors were polymerized using ammonia and methylamine. MADB and DADB are different from TADB in that one, or two, of the chlorines, respectively, attached to silicon are replaced by inert methyl groups. Due to the lower number of chlorine functions available for polycondensation, the resulting polymers show a smaller degree of crosslinking than the TADB derived polymers. For example, the polymer made from DADB and ammonia at room temperature is a soluble, highly viscous liquid, whereas the corresponding polymer of TADB is an insoluble solid.

In the first step of Equation 2-1, only one Si-N bond in HMDZ is cleaved by the silane $(\text{H}_3\text{C})_n\text{SiCl}_{4-n}$. At mild conditions, the elimination of the second trimethylsilyl group can only be achieved using the stronger Lewis acid BCl_3 . As a further member of this family of precursors, (trimethylsilylamino)di-chloroborane (TMDB) can be obtained by reaction of HMDZ with BCl_3 at very low temperatures.⁸⁰

A major advantage of this reaction path is involved in the formation of a volatile byproduct, e.g., chlorotrimethylsilane which can easily be distilled off. Furthermore, the yields are usually high, and the heats of reaction are low. Thus, reactions of this type can

be scaled up without any fundamental problems. It should be noticed that by reacting the byproduct chlorotrimethylsilane with ammonia, the educt hexamethyldisilazane can be recovered, which is of particular interest for environmental and economic reasons.

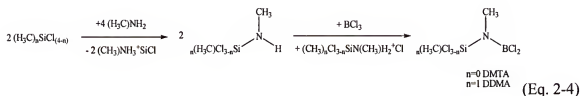
For the formation of element nitrogen bonds, stannazane cleavage is a widely applied alternative to the silazane cleavage. Since fission of the labile Sn-N bond proceeds much more smoothly, stannazanes are preferred when the reactivity of silazanes is not sufficiently high. A synthesis of a single source precursor solely utilizing stannazane cleavages is shown in Equation 2-2.^{81,82} If the second step of this reaction is carried out with equimolar amounts of BCl_3 and stannazane, the resulting dichloroboryl-trichlorosilyl-trimethyl-stannylamine cannot be isolated as such, but dimerizes spontaneously⁸² to a cyclic precursor containing silicon and boron in a 1:1 ratio (Equation 2-3).



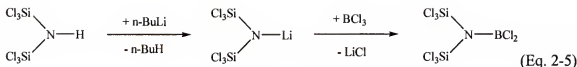
The precursors trichlorosilyl-dichloroboryl-methane (TSDM), dichloro(methyl)silyl-dichloroboryl-methane (DSDM), B,B'B''-trichlorosilylmethyl-borazine (TSMB),

B,B',B''-dichloro(methyl)silyl-methyl-borazine (DSMB), and $[(\text{Cl}_2\text{B})_2\text{NSiCl}_3]_2$ have been polymerized with both ammonia and methylamine, whereas dichloroboryl-methyl-trichlorosilyl-amine (DMTA), 1-(dichloroboryl)-1-(trichlorosilyl)-ethane (TSDE), and $\text{Cl}_2\text{BN}(\text{SiCl}_3)_2$ have only been reacted with the most promising crosslinking reagent methylamine.⁸²⁻⁸⁴ However, since organotin compounds are more or less toxic, depending on their degree of alkylation, the production of a precursor on an industrial scale using the stannazane route does not seem to be reasonable.

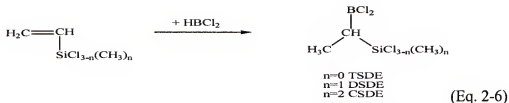
Recently, the well known dehydrohalogenation reaction has been employed to open the access to another family of single source precursors.⁸⁵ Using a gas phase reaction, dichloroboryl-methyl-trichlorosilyl-amine and dichloro-boryl-dichloro(methyl)silyl-methyl-amine, respectively, can be produced in high yields (Equation 2-4). As this synthesis can be performed in a continuous process and the appropriate educts are cheap, it is particularly well suited for scale up.



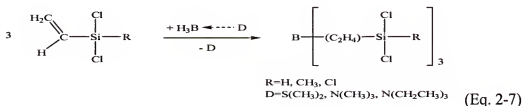
Transmetalation is also appropriate for creating boron-nitrogen bonds. Starting from molecules containing (acidic) NH functions, the nitrogen atom is readily metallated by n-butyl lithium. Subsequent reaction of the lithium amide with a suitable element halide provides the desired precursor, while the lithium halide is eliminated in Equation 2-5.^{82,86}



There are basically two reaction types of importance in the formation of carbon-boron bonds: hydroboration and transmetallation (salt elimination). An elegant route to alkylidihaloboranes has been introduced by Soundararajan and Matteson,^{87,88} who employed a mixture of trichloroborane and trialkylsilane to generate HBCl_2 in situ. This highly reactive intermediate hydroborates alkenes readily and in high yields, even at low temperatures. In 1997 Jansen and Jungermann applied HBCl_2 for the hydroboration of vinylchlorosilanes, and opened up a convenient access to a family of single source precursors containing a branched carbon bridge between boron and silicon in Equation 2-6.^{83,89}

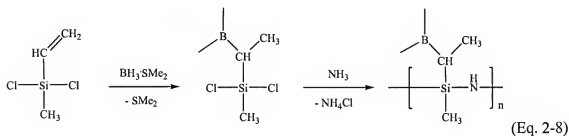


Based on the results of Riccitiello et al.,⁹⁰ who reported on the synthesis of polyborosilanes through hydroboration of methylvinylsilanes by borane adducts or diborane, Aldinger et al.,⁹¹ and Riedel et al.,⁹² applied the hydroboration reaction of different borane adducts with various vinylsilanes obtaining single source precursors with a carbon bridge between silicon and boron in Equation 2-7.



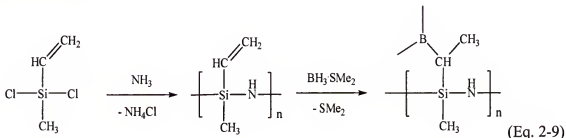
Polycondensation of tris[(dichloromethylsilyl)ethyl]borane with ammonia results in an organopolyborosilazane with 4 wt% boron content. The disadvantage of this procedure is the separation of the polymer from the byproduct ammonium chloride.^{6,93} Employing bis(trimethylsilyl)carbodiimide instead of ammonia elegantly leads to boron modified polysilylcarbodiimides. This has been found when using the single source precursors, tris[(dichloromethylsilyl)ethyl]borane, as well as its derivatives tris[(dichlorosilyl)ethyl]borane, and tris[(trichlorosilyl)ethyl]borane. The variation of the substitution patterns of the single source precursors gives polymers exhibiting significantly different amounts of crosslinking.^{91,94}

In order to understand the crosslinkage capabilities of the polymers, the reduction of mass loss during pyrolysis and salt-free polymerization have been investigated for different reaction routes. They are based on the either so-called ‘monomer route’ or the ‘polymer route’. The monomer route is characterized by the transformation of functionalized monomer units into a preceramic polymer (tris-methyldichlorosilyl-ethyl borane) yielding the boron modified polysilazane in Equation 2-8.

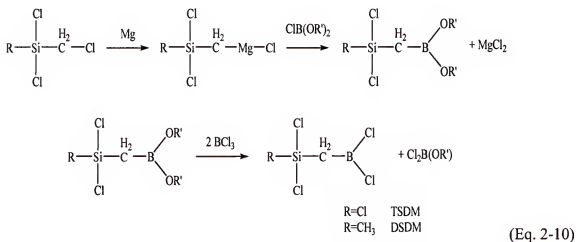


The polymer route is achieved by the functionalization of a polymeric precursor, e.g., hydroboration of polymethylvinylsilazane in Equation 2-9. The two reactions result in a highly crosslinked preceramic network and an increased ceramic yield. In particular,

the polymer route offers a very high yield and rapid reaction compared to monomer route. However, the separation of the polymer and ammonium chloride followed by two routes are very difficult.

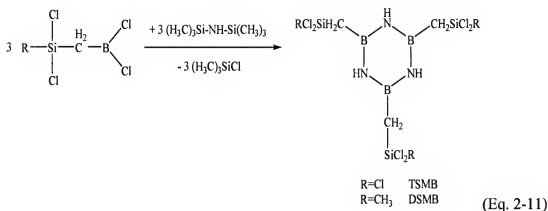


The most widely employed procedure for the preparation of such organoboranes is the well known Grignard reaction starting from a suitably substituted halogenoalkylsilane and magnesium. Subsequent reaction of the Grignard reagent with a haloborane leads to the desired organoborane in Equation 2-10.



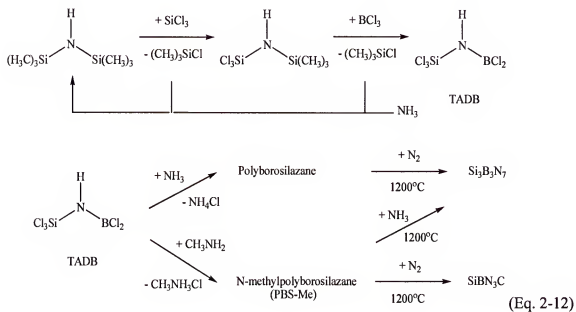
The direct reaction of the silicon Grignard reagent with a trihaloborane is hampered by severe obstacles. The preparation of the magnesium organyl can only be carried out using an ether as solvent (e.g., diethyl ether or THF). In addition, the trihaloborane acts as a strong Lewis acid reacting rapidly with ethers, even at low temperatures.⁹⁵ This conflict

can be resolved by using a haloborane with low Lewis acidity, e.g., a dialkoxyhaloborane. Subsequent halogenation of the organoborane dialkylester yields the desired compounds of single source precursors which are the first to contain a methylene bridge between boron and silicon.⁹⁶ By reacting these precursors with hexamethyldisilazane, the corresponding borazine derivatives form ring structure which is very strong and stable, as shown in Equation 2-11.⁹⁷



SiBN₃C ceramic was synthesized by pyrolysis of a preceramic N-methylpolyborosilazane (PBS-Me) made from the single source precursor Cl₃Si-NH-BCl₂. Sporn et al completed the ammonolysis of trichlorosilylaminodichloroborane (TADB) with ammonia or methylamine, followed by pyrolysis of polyborosilazane or PBS-Me.²⁰ Two different types of multinary systems were obtained from applying N₂ and NH₃ at high temperature. The multinary carbonitridic ceramics do not melt without decomposition. The polymer obtained by ammonolysis is principally unmelttable, whereas the viscoelastic properties of PBS-Me can be tailored by an appropriate heat treatment to be liquidable, melttable, soluble, or

unmeltable. This method led to high yield. However, the preparation of the final ceramic products were achieved with rather complex routes, as shown in Equation 2-12.



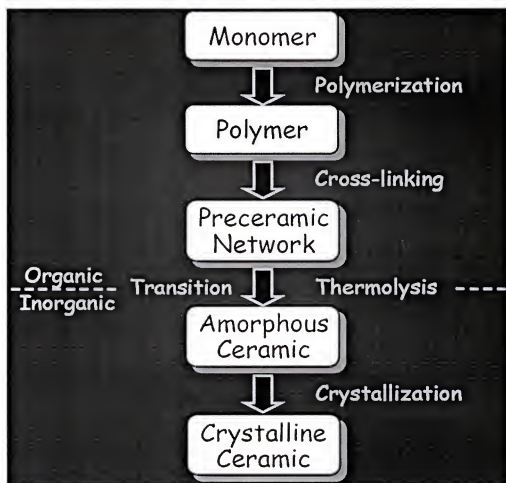


Figure 2-1. Schematic steps for fabrication of final ceramic from the synthesis of polymer precursor

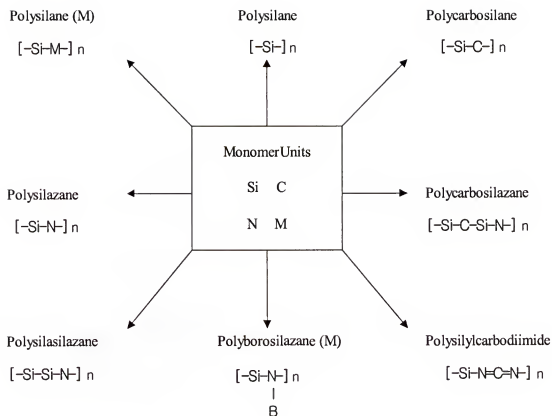


Figure 2-2. Type of backbone and functional side chains of precursor molecules

Table 2-1. Chronology of different types of polysilazanes

Precursors	Ceramics	Year
Polycarbosilazane	SiCN fibers	1974
Polycarbosilazane	Si ₃ N ₄ -SiC fibers	1975
Poly(silsequi-N-methylsilazane)	SiCN fibers	1982
Polyvinylsilazane	SiCN	1982
Poly(N-methylsilazane)	Si ₃ N ₄ -SiC fibers	1984
Polymethylsilazane	Si ₃ N ₄ -SiC fibers	1986
Polymethylsilazane	Si ₃ N ₄ +C	1986
Polysilazane	SiCN fibers	1987
Polyhydridodisilazane	Si ₃ N ₄ -SiC fibers	1987
Polyethylenesilazane	SiCN	1988
Polymethyldisilazane	Si ₃ N ₄ -SiC fibers	1988
Polysiladiazane	SiCN powders	1989
Polysilacyclobutasilazane	SiCN powders	1990
Octamethylcyclotetrasilazane	SiCN	1990
Polyborosilazane	SiBCN	1990
Polyvinylsilazane	SiCN powders	1991
Polydihydrosilazane	SiCN bulk	1992
Polymethylsilazane	Si ₃ N ₄ -SiC	1992
Cyclodisilazane	SiCN	1992
Polyborosilazane	SiBCN	1992
Polysilacyclobutasilazane	SiCN(O)	1992
Polycarbosilazane	SiCN	1993
Polyvinylmethylsilazane	SiCN powders	1993
Poly(hydrazinomethylsilane)	SiN(C _{0.5} H _{0.5})	1995
Poly(ureidosilazanes)	SiCN	1995
Polyvinylsilazane	SiCN bulk	1996
Polyborosilazane	SiBCN bulk	1996
Poly(disilazane)	SiCN	1998

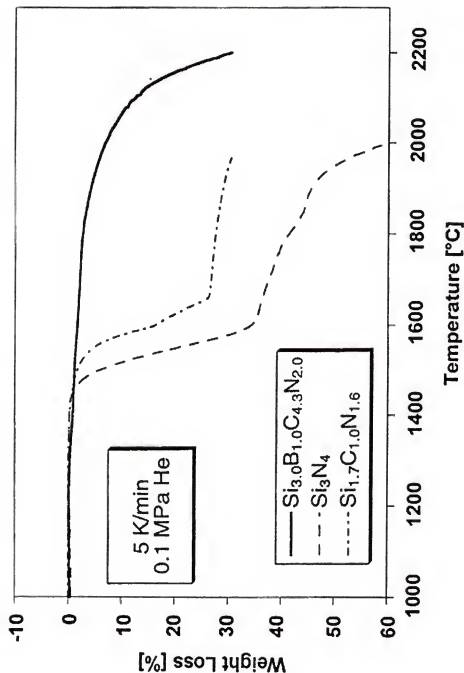


Figure 2-3. Comparison of TGA curves with a polycrystalline Si_3N_4 , SiCN and SiBCN

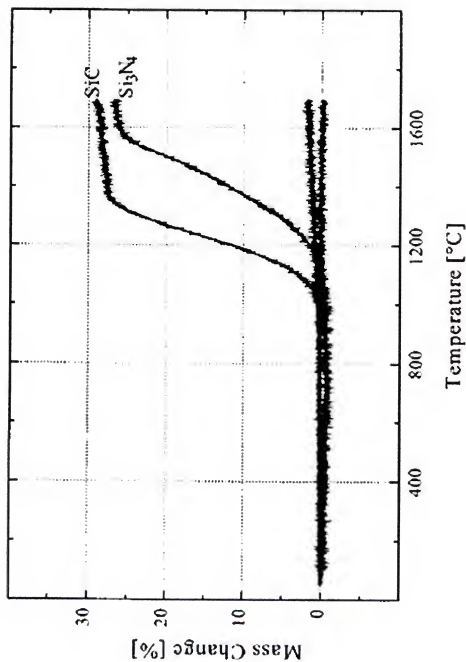


Figure 2-4. Oxidation behavior (TGA) of SiC, Si₃N₄, and SiBCN ceramics (Heating rate 5°C/min and flowing air)

Table 2-2. Survey of molecular single source precursors, derived polymers and ceramics

Single source precursor	Crosslinking reagent	Composition of the ceramic
$\begin{array}{c} \text{H} \\ \\ \text{Cl}_3\text{Si}-\text{N}-\text{BCl}_2 \end{array}$ <p>(Trichlorosilylamino)dichloroborane (TADB)</p>	Methylamine Ammonia	$\text{SiBN}_{2.3}\text{C}_{0.8}$ ("SiBN ₃ C") $\text{Si}_3\text{B}_3\text{N}_7$
$\begin{array}{c} \text{H} \\ \\ (\text{H}_3\text{C})\text{Cl}_2\text{Si}-\text{N}-\text{BCl}_2 \end{array}$ <p>(Methyldichlorosilylamino)-dichloroborane (MADB)</p>	Methylamine Ammonia	$\text{SiBN}_{2.8}\text{C}_{1.7}$ $\text{SiB}_{2.3}\text{N}_{1.4}$
$\begin{array}{c} \text{H} \\ \\ (\text{H}_3\text{C})_2\text{ClSi}-\text{N}-\text{BCl}_2 \end{array}$ <p>(Dimethyldichlorosilylamino)-dichloroborane (DADB)</p>	Methylamine Ammonia	$\text{SiB}_{3.8}\text{N}_{4.6}\text{C}_{3.3}$ $\text{SiB}_{1.3}\text{N}_{2.1}\text{C}$
$\begin{array}{c} \text{H} \\ \\ (\text{H}_3\text{C})_3\text{Si}-\text{N}-\text{BCl}_2 \end{array}$ <p>(Trimethylsilylamino)-dichloroborane</p>	Not investigated	Not determined
$\begin{array}{c} \text{H} \\ \\ ((\text{H}_3\text{C})_2\text{N})_3\text{Si}-\text{N}-\text{B}(\text{N}(\text{CH}_3)_2)_2 \end{array}$ <p>Tris(dimethylamino)silylamino-bis(dimethylamino)-borane (TABB)</p>	Cyanamide Guanidine Cyanguanidine Formamide Melamine	$\text{SiBN}_2\text{C}_{2.5}$ $\text{SiBN}_{2.5}\text{C}_2$ $\text{SiBN}_2\text{C}_{0.4}$ $\text{SiBN}_2\text{C}_{1.6}$ $\text{Si}_3\text{BN}_4\text{C}_2$
$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{Cl}_3\text{Si}-\text{N}-\text{BCl}-\text{N}-\text{SiCl}_3 \end{array}$ <p>Bis(trichlorosilylamino)-chloroborane (TACB)</p>	Ammonia	Not determined
$\begin{array}{c} \text{CH}_3 \\ \\ \text{Cl}_3\text{Si}-\text{CH}-\text{BCl}_2 \end{array}$ <p>1-(dichloroboryl)-1-(trichlorosilyl)-ethane (TSDE)</p>	Methylamine	$\text{Si}_2\text{B}_2\text{N}_5\text{C}_4$
$\begin{array}{c} \text{CH}_3 \\ \\ (\text{H}_3\text{C})\text{Cl}_2\text{Si}-\text{CH}-\text{BCl}_2 \end{array}$ <p>1-(dichloroboryl)-1-(dichloromethylsilyl)ethane (DSDE)</p>	Not investigated	Not determined
$\begin{array}{c} \text{CH}_3 \\ \\ (\text{H}_3\text{C})_2\text{ClSi}-\text{CH}-\text{BCl}_2 \end{array}$ <p>1-(dichloroboryl)-1-(dichloromethylsilyl)ethane (CSDE)</p>	Not investigated	Not determined
$\begin{array}{c} \text{Cl}_3\text{Si} \\ \\ \text{N}-\text{BCl}_2 \\ \\ \text{Cl}_3\text{Si} \end{array}$ <p>Dichloroboryl-bis(trichlorosilyl)amine</p>	Methylamine	$\text{Si}_2\text{BC}_2\text{N}_3$

CHAPTER 3 EXPERIMENTAL PROCEDURES

3.1 Synthesis

Polyborosilazane preceramic polymers were synthesized by three types of monomers following polycondensation reaction. The capacity of the reactor is 100mL. Small reactor volume gives an easy handling and a fast reaction time. In addition, it makes the synthesis oxygen-free atmosphere at a short time filling with inert gas into the reaction system. The monomer feed content is based on the reactor volume. Especially, the feed content of the solvent, hexane, was controlled in order not to exceed a half of total monomer content. However, a large volume of the solvent makes a proper reaction possible as the appropriate volume of solvent can prevent a radical reaction of the flammable and toxic monomers. The chemical data for various starting materials is listed in Table 3-1.

All of the monomers were handled without air contact and stored in a moisture-free environment. The boron trichloride (BTC), trichlorosilane (TCS), and hexamethyldisilazane (HMDZ) were purchased from Aldrich Chemical Co. and used without further purifications. BTC is very reactive, and therefore, it was maintained in a hexane solvent.^{98,99} The hydrolysis of the product was prevented using Schlenk-type glassware. In addition, the inner part of the reactor stayed in an inert atmosphere and the glassware was thoroughly cleaned and dried before synthesis. A vacuum was applied to the reaction system to remove the residual air and the system was subsequently filled

with nitrogen before adding monomers. In order to prevent contact with oxygen or water during chemical transfers, a syringe was used to make injections into the reactor.

Boron trichloride in 1M-hexane solution was introduced with a syringe from the bottle. The proper amount was weighed on a balance and injected into a dropping funnel with a septum. A trichlorosilane solution was added into the dropping funnel in the same manner. Dropwise addition achieved a homogeneous solution without precipitation; a sudden addition of the monomers could generate precipitation among the reactants.¹⁰⁰ Although the mixed solution became cloudy, no precipitation occurred. Nitrogen charging eliminated the possible influx of air during this mixing step. Meanwhile, the reactor remained at room temperature. HMDZ was added to the mixed solution dropwisely.⁹¹ Subsequently, nitrogen purging was performed for several minutes before heating.

From initial studies, the molar ratio between monomers was set at 1:1:4 (BTC:TCS:HMDZ). The reaction was initiated by slowly heating the reactor immersed in silicon oil bath. It was possible to observe the subsequent reactions through the transparent glass reactor while the reactor reached 200 °C. At around 70 °C, the reactor abruptly started boiling and the extracts were collected in a condensing device. A column on top of the reactor was wrapped with a heat band to separate the byproducts providing heat efficiency. Extracts removed from the reactor were gathered into flasks at various temperatures and identified by IR analysis. The unreactive monomers and byproducts that remained in the reactor at the maximum temperature reached were removed by application of a vacuum for 1 h. After the full elimination of any liquid phase, the product attached itself to the inner surface of the reactor in the shape of a white bulky substance.

A second nitrogen purge returned the reactor and its contents to room temperature. The bulk product was transferred into a glove box, placed in a vial full of nitrogen, and finally stored in vacuum dry-sealing desiccators.

3.1.1 Preparation of Preceramic Polymer

As described above, three different monomers are introduced in this experiment. Boron trichloride and trichlorosilane is evenly mixed with each other. BTC is very reactive and therefore it is maintained in a hexane solvent. Dropwise addition can achieve a homogeneous solution without precipitation; a sudden addition of the monomers could generate precipitation among the reactants. Nitrogen is purged to eliminate the possible influx of air during this mixing step. HMDZ and heat adds to start reaction.

From initial studies, the molar ratio between monomers is set at 1:1:4 (BTC:TCS:HMDZ). The reaction is initiated by slowly heating the reactor immersed in silicon oil bath. At the temperature of hexane solvent, the reactor abruptly starts boiling and the extracts are collected in a condensing device. A column on top of the reactor is wrapped with a heat band to separate the byproducts providing heat efficiency. Extracts removed from the reactor are gathered into flasks at various temperatures and identified by IR analysis. The unreactive monomers and byproducts that remained in the reactor at the maximum temperature reached are removed by application of a vacuum for 1 h. After the full elimination of any liquid phase, the product is collected in the reactor. A second nitrogen purge returns the reactor and its contents to room temperature. The bulk product is transferred into a glove box, placed in a vial full of nitrogen, and finally stored in vacuum dry-sealing desiccators.

3.1.2 Experimental Setup

Amorphous SiBNO ceramics with homogeneously distributed elements are supposed to form from polycondensation of perhydropolysilazane with boron methoxide. According to all current research, these oxidenitrides are inferior to the purely nitridic and carbonitridic ceramics with respect to their mechanical properties. Synthesis of oxide ceramics is not restricted by chemical apparatus as they are prepared under normal atmosphere. However, it is most important to prevent the influx of oxygen during synthesis, even in a further fabrication. Oxides can be formed by contact with oxygen and moisture-rich conditions, inevitably. Such a hydrolysis of the oxide-free products can be prevented using Schlenk-type glassware, which maintains an inert reaction system and effectively eliminates byproducts, shown in Figure 3-1. The glassware is thoroughly cleaned and dried before synthesis. A vacuum is applied to the reaction system to remove the residual air and the system is subsequently filled with nitrogen before adding monomers. In order to prevent contact with oxygen or water during chemical transfers, a syringe is used to make injections into the reactor.

More specific feature of the reactor is shown in Figure 3-2. 3-neck flask is utilized to give addition, condensation, and discharge. In the use of oil bath, a stepwise evolution of the reaction can be observed during synthesis. All monomers are inserted into the left branch of the reactor dropwisely by using stopcock, which can isolate the oxygen-free system from the surrounding and control the inert gas and the extracts. The middle branch is connected with condensing device, which collects the extracts by condenser at the top of the column with flowing cooling water. The vent line is located at the right branch, which can be possible to bypass the inert gas for the storage of the obtained product after cooling.

3.1.3 Modification of Preceramic Polymers by Changing Reaction Variables

After identification of the first precursor obtained in our project, the modification of the precursor, its conditions and purposes are outlined in this section.

3.1.3.1 Change of synthetic conditions

Increase molar ratio of the monomer hexamethyldisilazane (HMDZ). The reaction starts with addition of HMDZ and heat. The increase of molecular weight can be also propagated by formation of HMDZ during synthesis. Therefore, the function of HMDZ in the reaction is an initiator and crosslinking agent. HMDZ is able to substitute chlorine at first stage attaching trimethylsilylamino groups to the main chain. With a further stage, HMDZ is formed by eliminating residual chlorine. Total six chlorines attached to boron and silicon can be removed through different reaction routes. A few molecules remain short chains but others continue to propagate. Unreactive HMDZ is removed at its boiling point (127 °C). The increase of HMDZ affects the reactivity and the molecular weight. It can be assumed that there is a critical HMDZ content to accomplish the reaction. Thus, the HMDZ content was increased at molar ratio up to 1:1:6 (BTC:TCS:HMDZ).

Temperature. The reactivity and the yield of precursor are directly related to reaction temperature. The reaction is accelerated by the liberation of HMDZ that has a boiling temperature of 127 °C. The maximum reaction temperature reached from 127 °C to 300 °C. Elimination of byproducts and yield of the products was assessed by collecting them into Schlenk flask.

3.1.3.2 Change of starting materials

Polyborosilazane preceramic polymer was modified by a change of pendant group attached to silicon. One of the purposes in this approach is to verify the effect on the size of pendant groups attached to silicon site of trichlorosilane (TCS) monomer. The second purpose is to increase the carbon content into the amorphous network by choosing longer alkyl chains, as terminal alkyl groups react with HMDZ being able to form silicon-carbon bridges during synthesis. Lastly, the purpose is to identify the processibility of the precursors and the solubility on the solvents by introduction of bulkier side groups into the silicon branch. It may allow the final ceramic to enhance mechanical properties due to large carbon content and benzene crosslinkage between silicon molecules. One of the starting materials, trichlorosilane (HSiCl_3) was replaced by methyltrichlorosilane (CH_3SiCl_3), ethyltrichlorosilane ($\text{C}_2\text{H}_5\text{SiCl}_3$) and phenyltrichlorosilane ($\text{C}_6\text{H}_5\text{SiCl}_3$).

3.2 Pyrolysis

Prior to the pyrolysis, the polymer was ground to increase the powder surface area in contact with a nitrogen or an argon environment. The compositional and structural changes of the preceramic polymer were simultaneously investigated under various thermal treatments. The preceramic polymers was partially pyrolyzed based on TGA, as shown at the top of Figure 3-3. Pyrolysis was performed by heating from room temperature to a given temperature under a nitrogen gas at a heating rate of $10^\circ\text{C}/\text{min}$, holding at a given temperature for an additional 60 min, and then finally cooling at approximately $30^\circ\text{C}/\text{min}$ to room temperature.¹⁰¹ To guarantee the prevention of hydrolysis during pyrolysis, additional argon purging line was built into the thermal

analysis system, which contains the small crucible chamber. For heat treatments conducted at 1000 °C to 1600 °C, a high temperature furnace was used.

The furnace setup at the bottom of Figure 3-3 is Thermolyne F59348CM furnace capable of reaching a temperature of 1700 °C and with a heat zone of approximately 6 inches, variation of temperature within the heat zone is about ± 10 °C. The furnace tube is a 99.98% alumina tube needed for pyrolysis process. Vacuum of up to 1×10^{-3} torr can be achieved via the use of a roughing pump (Marvac Scientific). Control of the gas flow was provided by an MKS mass flow meter/controller. In case of reducing environment experiments, the oxygen content of the ultra-high purity gases to be used can be further reduced via insertion of oxygen gathering system in between the MFM/MFC and the furnace tube. The oxygen content of the gases used was further monitored via an oxygen sensor during pyrolysis. Initially, the furnace tube was both flushed with high purity argon and repeatedly purged by a vacuum at room temperature. Before pyrolysis, an oxygen analyzer attached to the outlet of the tube measured the oxygen content in the tube furnace.

The condition of pyrolysis was followed by the same route used for pyrolysis below 1000 °C. Subsequently, spreading a polymer powder over an alumina combustion boat is maximized by the contact area of the samples with heat during pyrolysis. The heat treatment was also performed for different exposure times (1 to 12 h) at 1600 °C. The specimens was also heated at a rate of 10 °C/min and cooled at a rate of 30 °C/min. The pyrolyzed polymer was stored in a vacuum dry-sealing desiccator. The desiccator was repeatedly pumped for storage.

3.3 Characterization

Polymer structures we deduced in detail primarily using Fourier Transform Infrared spectroscopy (FT-IR) and magic angle spinning nuclear magnetic resonance spectroscopy (MAS-NMR), and x-ray diffraction spectroscopy (XRD). Existence of chemical composition was shown by elemental analysis (EA), atomic absorption spectroscopy (AA), and energy dispersive x-ray spectroscopy (EDS).¹⁰² Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out for thermal behavior and structural changes as a function of temperatures. Experimental details of each method are described in the following section.

3.3.1 Characterization of Preceramic Polymers

3.3.1.1 Infrared (IR), nuclear magnetic resonance (NMR), and x-ray diffraction (XRD) analysis

IR analysis. IR analysis was used to identify the final polymer structure, which may form the expected bonds after synthesis and pyrolysis of the preceramic polymer at various temperatures. An OMNIC FT-IR Spectrometer recorded the FT-IR spectra. The diffuse-reflectance IR spectra (DRIFT) and transmittance IR spectra of the preceramic polymer powder were obtained using a KBr pellet disc. The attenuated total reflectance infrared (ATR/IR) spectroscopy provided valuable information on the removal of the extracts. All experiments were performed under a slight nitrogen flow to prevent hydrolysis during the IR analysis. In particular, the effect of long-term exposure to elevated temperatures and the influence of hydrolysis were evaluated. Figure 3-4 shows OMNIC FT-IR spectrometer. The sample box in the main instrument was purged by nitrogen gas before analysis.

NMR analysis. Solid-state NMR spectroscopy was utilized to determine a local sequence of the bulky molecule in the amorphous structure of polyborosilazane preceramic polymer. ^{29}Si , ^{13}C , ^{11}B , ^1H , and ^{15}N -NMR spectroscopic series probe their local sequence after synthesis. Polyborosilazane preceramic polymer was difficult to be dissolved in any of organic or inorganic solvents. Therefore, MAS-NMR spectroscopy was applied to investigate the structure of the preceramic polymer powder. MAS-NMR spectrometer is shown in Figure 3-5. NMR spectra were obtained on a 400 MHz Avance Bruker CXP 300 spectrometer by using a 4.0 mm triple resonance probe at a static magnetic field of 7.05 T. The ^{29}Si , ^{13}C , ^{11}B , ^1H , and ^{15}N frequencies were 79 MHz, 100 MHz, 128 MHz, 400 MHz, and 41 MHz, respectively.¹⁰³

^{29}Si , ^{13}C , and ^{11}B -NMR spectra were recorded with a sample spin rate of 6.0 kHz and either a single pulse or a cross polarization (CP) excitation of $\pi/2$ pulse widths of 5 μs (^{29}Si , ^{13}C , and ^{11}B). In single pulse excitation experiments, ^{29}Si , ^{13}C , and ^{11}B -NMR spectra were obtained by using a decoupling power of 7 dB, 3-ms contact pulse and recycle delays between 2 and 4 sec. ^{29}Si , ^{13}C , and ^1H chemical shifts were referenced to tetramethylsilane (TMS) as an external standard. ^{15}N and ^{11}B chemical shifts were determined relative to NH_4OH and H_3BO_3 . ^1H -MAS NMR spectra were recorded at sample spinning rate of 12 kHz and single pulse excitation ($\pi/2$ pulse width of 4 μs) with a recycle delay of 2 sec.

XRD analysis. A Philips APD 3720 XRD identified the structural changes and potential phase transformations of the preceramic polymer at elevated temperatures. The scanning angle (2θ) was set at 10 to 80° . A monochromatic CuK_α radiation was used with a wavelength of $\lambda/2=154.06$ pm. The pyrolyzed precursors at different temperatures were

also be studied. Structural changes of these materials were performed at different holding times (1 to 12 h). A simple XRD spectrometer is shown in Figure 3-6.

3.3.1.2 Elemental analysis (EA), atomic absorption spectroscopy (AA), and energy dispersive spectroscopy (EDS) analysis

EA. The composition of both preceramic polymers and pyrolyzed polymers was analyzed by using an EA-1108 Elemental Analyzer. For the analysis of carbon, nitrogen, and hydrogen, high-temperature combustion method is introduced. As shown in Figure 3-7, the combustion of the samples is completed in an inert gas chamber.

AA (or AAS). Atomic absorption spectroscopy (AA) uses the absorption of light to measure the concentration of gas-phase atoms. Since samples are usually liquids or solids, the analyte atoms or ions must be vaporized in a flame or graphite furnace. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption. Applying the Beer-Lambert law directly in AA spectroscopy is difficult due to variations in the atomization efficiency from the sample matrix, and nonuniformity of concentration and path length of analyte atoms (in graphite furnace AA). Concentration measurements are usually determined from a working curve after calibrating the instrument with standards of known concentration.

The fusion technique characterizes the contents of silicon (Si) and boron (B) in the preceramic polymer or ceramic structure. The preceramic polymer powder was converted into soluble forms of silicon or boron analyzing the solutes for total element.¹⁰² In their elemental form, each atoms will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular element by focusing a beam of UV light at a specific wavelength

through a flame and into a detector. The sample of interest is aspirated into the flame (Figure 3-8). If a detective element is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity.

EDS. The presence of impurities in preceramic polymer was examined by JEOL JSM-6400 EDS. The polymer powder was coated with carbon or gold in order to alleviate the random perturbation of the secondary electrons coming from preceramic powder in the vacuum chamber. EDS system can detect x-ray from all the elements in the periodic table above beryllium, $Z=4$, if present in sufficient quantity. With a minimum detection limit of 100 to 200 ppm for most elements, an EDS system (Figure 3-9) is capable of detecting less than a monolayer of film on a substrate using $K\alpha$ lines at moderate accelerating voltages of 5 to 15keV. Therefore, EDS is a very simple technique for obtaining special value from a coated layer on the substrate.

3.3.1.3 Thermal analysis

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out using TA Instruments SDT 2050 to observe both weight loss and heat flow of the preceramic polymer at a heating rate of 10 °C/min in an inert atmosphere. In TGA measurements, the mass of the sample is recorded continuously while temperature is increased at a constant rate. Weight losses occur when volatiles absorbed by the polymer are driven off and at higher temperatures when degradation of the polymer occurs with the formation of volatile products. In the DSC, the sample and reference are provided with independent heaters. DSC equipment measures the heat flow by maintaining a thermal balance between the reference and sample by changing a current passing through the heaters under the two chambers.

The heating of a sample and reference proceeds at a predetermined rate until heat is emitted or consumed by the sample. If an endothermic occurrence takes place, the temperature of the sample will be less than that of the reference. Excess current is fed into the sample compartment to raise the temperature to that of the reference. The current necessary to maintain a constant temperature between the sample and reference is recorded. The area under the resulting curve is a direct measure of the heat of transition. In general, a change in T_g , T_m , and T_c can be obtained from DSC curve, which is an evidence of the transition in the preceramic polymers. TA Instruments SDT 2050 in Figure 3-10 give the data for weight loss and heat flow, simultaneously.

3.3.2 Characterization of Pyrolyzed Polymers

With the same characterization techniques, the structural change of the pyrolyzed polymers was identified at different temperatures. The phase transformation from amorphous and crystalline was detected by XRD analysis. AA and EA analysis identified the compositional changes.

3.4 Autoclave Test

3.4.1 Autoclave

Polyborosilazane preceramic polymer was placed in an autoclavable tray with sides that are 5 inches in height. The use of trays should eliminate anything boiling over and spilling into the autoclave. The sample must fit within this tray. Therefore, polyborosilazane preceramic polymer was fabricated in the form of a pellet. Deionized water to be autoclaved must be in an autoclavable vessel that is at least twice as large as the volume to be autoclaved.

A hydrothermal condition was maintained in the autoclave to give the condition similar to the nuclear environment at 350°C and 3000 psi for 24 h in water. The water

vaporized during the autoclave cycle to allow better penetration of stream into the sample. After autoclave, the remaining water was collected into the vial and analyzed by ICP. Autoclave tester is shown in Figure 3-11.

3.4.2 Inductively Coupled Plasma (ICP) Analysis

Inductively coupled plasma (ICP) analysis requires that the elements which are to be analyzed should be in solution. An aqueous solution is preferred over an organic solution, as organic solutions require special manipulation prior to injection into the ICP. Solid samples are also discouraged, as clogging of the instrumentation can occur. The nebulizer transforms the aqueous solution into an aerosol. The light emitted by the atoms of an element in the ICP must be converted to an electrical signal that can be measured quantitatively. This is accomplished by resolving the light into its component radiation (nearly always by means of a diffraction grating) and then measuring the light intensity with a photomultiplier tube at the specific wavelength for each element line.

The light emitted by the atoms or ions in the ICP is converted to electrical signals by the photomultiplier in the spectrometer. The intensity of the electron signal is compared to previous measured intensities of known concentration of the element and a concentration is computed. Each element will have many specific wavelengths in the spectrum which could be used for analysis. Thus, the selection of the best line the analytical application in hand requires considerable experience of ICP wavelengths.

The Perkin-Elmer Plasma 3200 Inductively Coupled Plasma Spectroscopy (ICP) system (Figure 3-12) is equipped with two monochromators covering the spectral range of 165 to 785 nm with a grating ruling of 3600 lines/mm. The ICP is operated on the principle of atomic emission by atoms ionized in the argon plasma. Light of specific wavelengths is emitted as electrons return to the ground state of the ionized elements,

quantitatively identifying the species present. The system is capable of analyzing materials in both organic and aqueous matrices with a detection limit range of less than 1 ppm. The amount of boron extracted from polyborosilazane preceramic polymer during autoclave test was measured.

Table 3-1. Chemical properties of monomers and their feed contents

Chemical	Mol	Molar ratio	M.W (g)	ρ (g/mL)	Purity (%)	Net vol. (mL)	Net wt. (g)
Trichlorosilane	0.03	1	135.5	1.342	98	3.1	4.2
Methyltrichlorosilane			149.5	1.273	97	3.6	4.6
Ethyltrichlorosilane			163.5	1.238	99	4.0	5.0
Phenyltrichlorosilane			211.6	1.321	95	5.1	6.7
Boron trichloride	0.03	1	117.2	0.738	100	30.0	22.2
Hexamethyldisilazane	0.12	4	161.4	0.774	97	25.8	20.0
Hexane	-	-	86.0	0.659	100	25.3	-

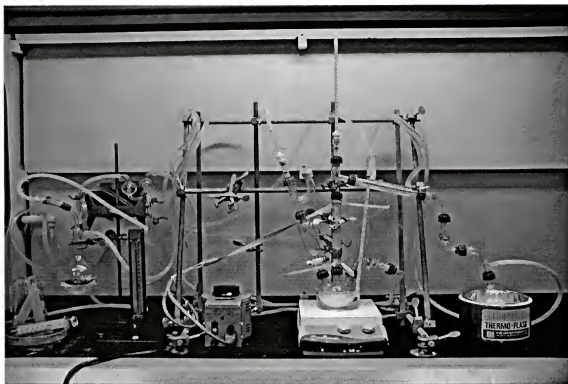


Figure 3-1. Glassware setup for synthesis of polyborosilazane preceramic polymers

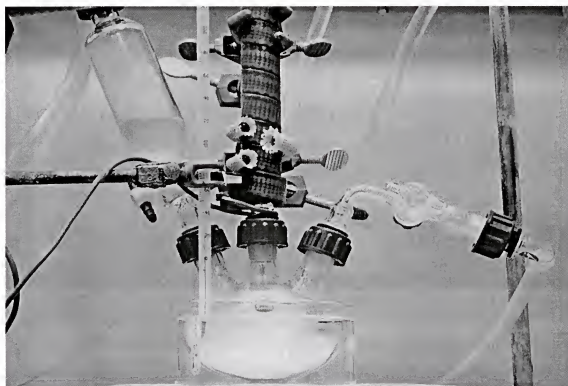


Figure 3-2. Reactor parts during the synthesis of polyborosilazanes preceramic polymers

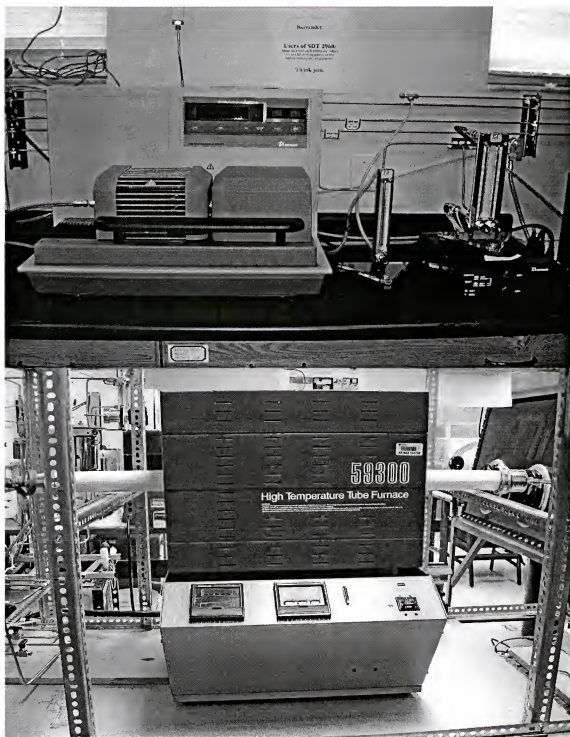


Figure 3-3. Furnace setup for pyrolysis of polyborosilazane preceramic polymers



Figure 3-4. OMNIC FT-IR spectrometer

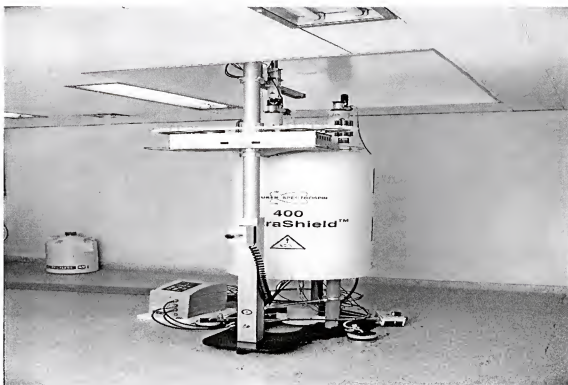


Figure 3-5. MAS-NMR spectrometer (400 MHz Avance Bruker CXP 300)

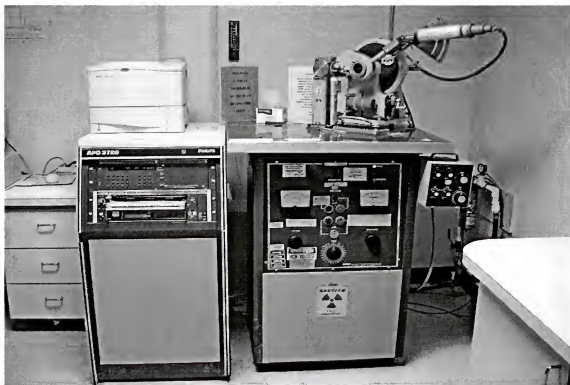


Figure 3-6. X-ray diffraction spectrometer (Philips APD 3720 XRD)

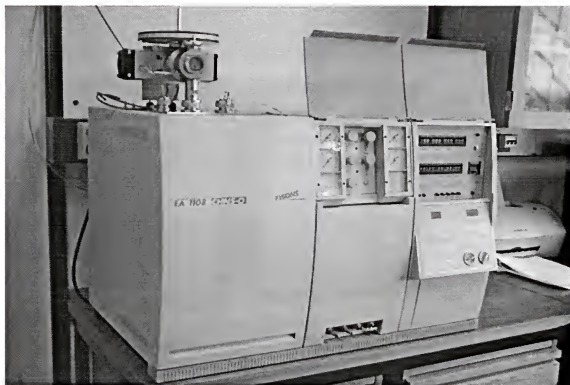


Figure 3-7. EA-1108 Elemental analyzer

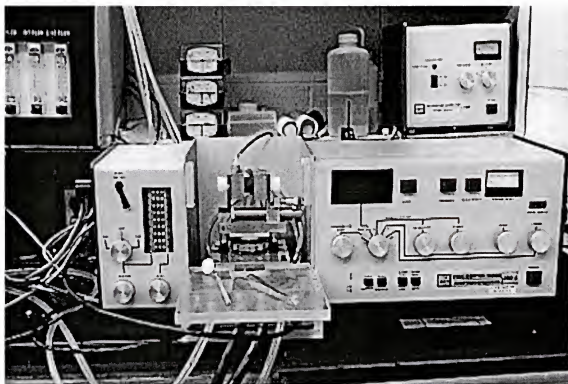


Figure 3-8. Atomic absorption spectrometer

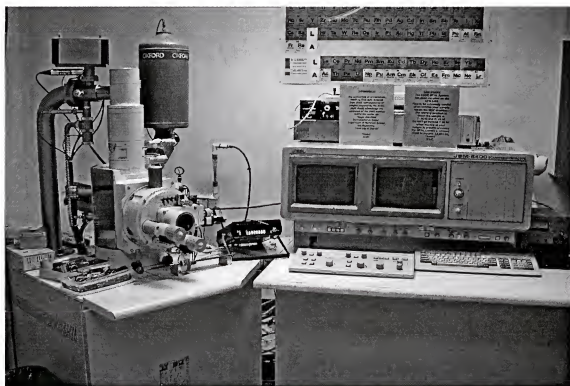


Figure 3-9. JEOL JSM-6400 EDS

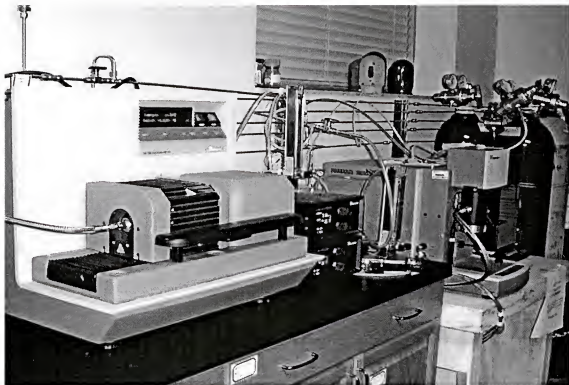


Figure 3-10. TA Instruments SDT 2050

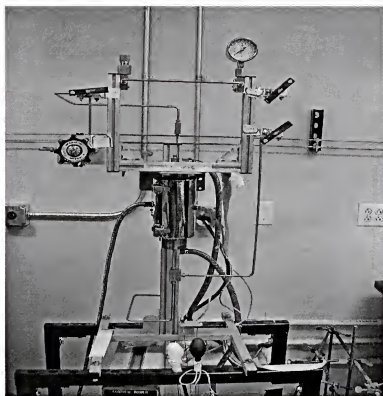


Figure 3-11. Autoclave tester



Figure 3-12. Perkin-Elmer Plasma 3200 ICP

CHAPTER 4

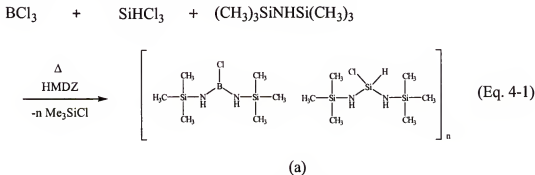
RESULTS AND DISCUSSION

This chapter presents and discusses the experimental results from synthesis, characterization, modification, pyrolysis, and application. The synthesis route of polyborosilazane preceramic polymer follows the hypothesis. All the characterization techniques are focused on the confirmation of the proposed structure. The analytical results of the spectroscopic and thermal characterization, processing, and development of a novel polyborosilazane preceramic polymer will be presented first. Results related to the pyrolysis process and the pyrolyzed ceramics will be described subsequently. The results will validate the hypothesis given in the following section. Discussion will also give attention to the confirmation of the hypothesis. Durability of the polymer is evaluated by autoclave testing, which has an environment similar to the failure of the nuclear reactor assemblies.

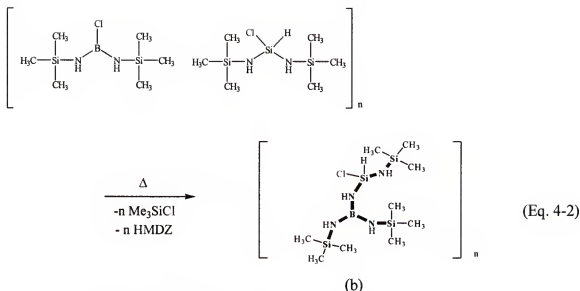
4.1 Hypothesis on Chemical Mechanism

Molecular components of silicon and boron can be incorporated in non-oxide ceramics using a single source route, and bear functionalities that can be polymerized by many synthesis processes. Through a single source route, they offer the opportunity for inserting nitrogen and carbon to achieve thermal and mechanical properties at high temperatures. Furthermore, in the field of materials research aimed to large-scale applications, the molecular precursors should be easily available and inexpensive. To accomplish this purpose, a novel synthesis route is introduced into our research.

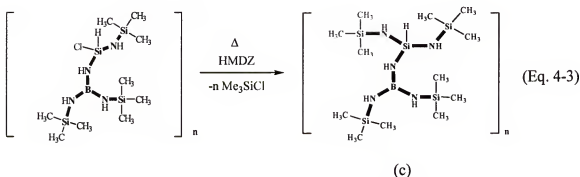
Borontrichloride (BTC) and trichlorosilane (TCS) can be used to give the functionality, which have three chlorine functional groups, respectively. Initially it allows that the molar ratio between BTC and TCS is equal. From the structural point of view, a crucial subject is a homogeneous distribution of the elements in the precursor. It is expected that HMDZ could attack the chlorine of borontrichloride and trichlorosilane equivalently. Under this assumption, it is possible to complete the chemical reaction and the reactants can form the intermediate product that corresponds to the intermediate molecule in the process of synthesis as shown in Equation 4-1.



At the above reaction step, the chlorine atoms of the intermediate molecules (a) may be removed by a condensation reaction with each other leaving and/or forming chlorotrimethylsilane¹⁰³ and hexamethyldisilazane at an elevated temperature. In contrast to such a reaction, hexamethyldisilazane as a reactant at this time attacks the chlorine producing an intermediate structure again, shown in Equation 4-1. Consequently, the intermediate molecule (a) is formed as a product in the unstable form. Since the boron halide at the left side of the intermediate molecule (a) can be easily attacked by Lewis base adducts rather than the silicon at the right side of the intermediate molecule (a), the additional reaction of the left compound is preferable. Therefore, the reaction between the molecules of intermediate (a) may be possible to form intermediate (b). (Equation 4-2)



With this reaction, the chlorine attached to the boron molecule is substituted. However, the chlorine at the silicon still remains. The chlorine attached to the silicon may be attacked by HMDZ and form intermediate molecules (c). (Equation 4-3)



The intermediate molecules (c) can be reacted with each other by the formation of boron-nitrogen bonds eliminating the end groups in the molecules during a self-condensation reaction. In consequence of this reaction, intermediate compounds grow in stages at an elevated temperature and form an amorphous polymer structure at the end, as shown in Figure 4-1.

As a structural feature, the preceramic polymer contains a nitrogen bridge between silicon and boron. In case of conventional synthesis methods, ammonia (NH_3), methylamine (CH_3NH_2) and Harrod-type catalysts (Cp_2TiR_2 ; $\text{R}=\text{Me}$, OC_6H_5) have been utilized as crosslinking agents.^{55,104} The crosslinking reaction can occur by ammonolysis and transmetallation (salt elimination) for creating boron-nitrogen bonds. In our study, hexamethyldisilazane (HMDZ) was reacted with both borontrichloride and trichlorosilane simultaneously as shown in Equation 4-1. At the initiation step, HMDZ is first consumed. As the reaction is propagated, HMDZ is produced by salt elimination, which bridging silicon and boron, as it behaves as a crosslinking agent. Therefore, no additional crosslinking agent is necessary to form SiBCN-containing preceramic polymer. In addition to that, it will not be needed to remove the byproducts during synthesis. To verify the hypothesis, the characterization techniques were focused on IR and MAS-NMR.

4.2 Synthesis of Polyborosilazanes by Polycondensation

Synthesis of polyborosilazanes begins with a hypothesis about the reaction mechanism. As described in the previous section, the synthesis route is based on two monomers that have chlorine atoms as functional groups. Borontrichloride (BTC) and trichlorosilane (TCS) react with hexamethyldisilazane (HMDZ) via polycondensation. The corresponding reaction follows the stepwise kinetics. It refers to polymerization in which the polymer's molecular weight increases in a slow, steplike manner as reaction time increases.

At the initial stage, it is shown that the reactor is full of low molecular weight clusters with a C-Si-B-N main chain sequence. By a slight increase of the temperature to

200 °C, branching is accompanied with crosslinking. The reaction is accelerated by the subsequent liberation of HMDZ. It is speculated that the clusters observed in the bulky structure may form an extended amorphous structure together with neighboring clusters. During the elimination of the byproducts in a vacuum, the polymer precipitates from the solution with a subsequent increase in the molecular weight of the product and its high crosslinkage by intermolecular reactions.¹⁰⁵ Until the end of the reaction, the prevention of hydrolysis can be achieved under full control without oxygen. At the same time, byproducts were very carefully eliminated without any residue. The reactivity was not directly related to initial feed volume and final yield. The final product was a white bulky powder. In some cases, vacuum was applied to get a final solid product.

4.2.1 Evaluation of the Reactivity with Different Monomers

In a typical reaction, a solution of either trichlorosilane and borotrichloride was charged under a nitrogen atmosphere into a 100 mL reactor, which was previously evacuated at room temperature. After the completion of adding HMDZ, the mixture was heated in an oil bath. Extracts were gathered into the small flask passing through a distillation column. Propagation reaction was substantially started by increasing the temperature of the reactor, not by an addition of HMDZ. To prevent agglomeration of the solution, stimulated by a sudden reaction with the HMDZ, the reaction temperature was increased step by step at the beginning. Thus, the reactants are consumed without any long chains being formed throughout the system until the reaction progresses toward total reaction of the chains with themselves.

As the reaction proceeded, the setting temperature of the heater became much higher at a short period. Abrupt boiling was followed by the elimination of hexane

solvent at 69 °C. Heat was still added up to 127 °C for eliminating HMDZ with no further reaction observed around 127 °C. Among the modified polyborosilazane preceramic polymers, PCP4 shows the fastest reaction rate. It is due to a highly reactive benzene ring attached to the phenyltrichlorosilane molecule. Even though all the yields in modified precursors are high, the yield of PCP4 is higher than other modified precursors, which has 91.2%, as summarized in Table 4-1.

The maximum reaction temperature was increased from 127 °C to 300 °C, which is beyond the boiling point of HMDZ (127 °C). However, there is no difference in the result after the reaction temperature changes, except the volume extracts increase and the reaction time reduces. From IR analysis, no peak intensity changes is shown. It is expected that molecular weight (M_n or M_w) and molecular weight distribution (MWD) may be affected by the change of the reaction temperature. However, preceramic polymers lose significant mass during pyrolysis. For ceramic applications, the quantity of material obtained from the synthesis of polymer may not depend significantly on the starting molecular weight, but may depend instead on the constituents and bonding forces in the structure. It is reported that the thermal property of SiBCN ceramics obtained from borazine polymers is heavily dependent on the final silicon content and the number of boron and nitrogen bond, while the molecular weight in the precursor state is less affected.^{17,26,102}

An introduction of the starting monomer with bulkier side groups was designed to offer a large free volume in the polymer structure. For example, a phenyl group was introduced instead of hydrogen attached to silicon in trichlorosilane. The large side groups in the polymer chains allow easy access of neighboring molecules to them,

resulting in the possible crosslinking between nitrogen and silicon. Therefore, monomer change should provide the whole ceramic structure with the possibility of a strong bond formation. Furthermore, the processibility of the preceramic polymer is facilitated by the large free volume in the structure that prevents chain arrangement due to the steric hindrance. The final structure becomes much amorphous, which may allow a dense packing and a better solubility.

A selective synthesis approach was employed in our research. A change in the molar ratio of HMDZ promotes structural modification. For a comparison of the change in the molar ratio, only the molar ratio of PCP1 was varied with the content of HMDZ. The change was combined with the increase of HMDZ from 4 mol to 6 mol. The amount of HMDZ substitutes for all 6 chlorines in TCS and BTC during polymerization. The yield of final product was almost similar to the yield obtained from the original 1:1:4 molar ratio. However, the change in the molar ratio of HMDZ showed a very fast reaction rate. With the increase in the molar ratio of HMDZ, the final product did not convert its phase into powder. Rather, it remained in a gel state, which is very interesting. To remove byproducts effectively, a vacuum pump was used at the end of the reaction.

Despite the increase of the maximum reaction temperature near 300 °C in order to transform a gel phase into a solid phase of the final product, no transformation in the phase happened. It is expected that the increased content of HMDZ in the molar ratio substituted for all chlorines in TCS and BTC will subsequently form an extensive crosslinked network with the silicon and nitrogen bond in the shape of gelation at short times. Two different products obtained from the change in the molar ratio of HMDZ were investigated by spectroscopic and thermal measurements. The effect of modification on

the polyborosilazane preceramic polymer is evaluated and compared with each other at the following sections.

4.2.2 Evaluation of Hydrolysis during Polymerization

It has been recognized that one of the possible problems is the hydrolysis of the oxygen-free polyborosilazane. The other problem is the difficulty in the elimination of undesirable byproducts such as ammonium chloride that could remain after filtration. The critical drawback of nitrogen-containing polymers is their susceptibility to hydrolysis. Oxygen could unexpectedly accumulate in the system during synthesis, transferring, grinding, and pyrolysis. Since hydrolysis is a typical form of degradation, the reaction of oxygen-free polyborosilazane needs to be performed using a special controlled atmospheric technique. It is not easy to detect the precise amount of oxygen of an air-sensitive SiBCN preceramic polymer in a normal atmosphere. Therefore, the analysis of the oxygen content was not performed but estimated by the IR analysis.

Overlapping between peaks makes the interpretation of the IR spectrum difficult. In general, an IR spectrum below 1000 cm^{-1} normally does not contain readily identifiable peaks. However, it is possible to acquire IR spectra of hydroxyl-containing compounds without seeing a broad signal. Identification of a specific bond formation can often be confirmed by a comparison with a known spectrum. For example, the powder samples were deliberately treated after the hydrolysis of the product. First, one of the samples was obtained by exposing the preceramic polymer to a normal atmosphere for 3 days. However, the other sample underwent hydrolysis at high temperature under air cover.

Figure 4-2 shows the IR spectra of the selected samples. At approximately 3500 cm^{-1} , the peak broadening is more remarkable as the hydrolysis of the preceramic polymer increases. This data explains the formation of bond units with a silicon and

hydroxyl group in the molecule. The samples shown in Figure 4-2 exhibit a strong peak at the 1090 cm^{-1} region that does not appear in the preceramic polymer, which indicates the formation of a Si-O-Si bond. At 2156 cm^{-1} , the large peak assigned to a Si-H bond decreases in band intensity and then disappears after exposure to high air temperatures. Carbon oxidation is predominant at the initial stage with respect to exposure of the preceramic polymer under a normal atmosphere.

At higher temperatures the Si-C bond oxidation rate is comparable to the rate of oxidation of carbon. This allows a silica-like surface to build up on the SiBCN polymer, which slows all subsequent reactions due to the necessity to diffuse O_2 in and CO_x out of the bulk. Due to the interaction between plenty of hydrogen at the end of an amorphous chain and moisture-rich air, a similar hydrolysis also occurs at 2956 cm^{-1} . Compared to (b) and (c) in Figure 4-2, the IR spectrum of the preceramic polymer in Figure 4-2 (a) has no peak broadening as well as no peaks assigned to the absorption of an oxygen bond. As a result, it can be estimated that the preceramic polymer obtained from synthesis does not experience any hydrolysis. With this respect an unforeseen feature makes SiBCN superior to all known carbides and nitrides.

Figure 4-3 shows the IR spectra on the degree of hydrolysis of the samples with a different exposure environment and the exposure period. Sample (a) in Figure 4-3 was stored in a vacuum desiccator for 30 days without oxygen. The desiccator was periodically applied with vacuum to ensure the reliability of the storage without hydrolysis. Samples (b) to (e) were exposed to a normal atmosphere in the storage chamber. The average relative humidity and temperature in the chamber were maintained at the levels of 65% RH and $21\text{ }^\circ\text{C}$, respectively. The extent of hydrolysis for materials

after one month is shown in Figure 4-3 with (a) through (e) of IR spectra. The sharp peak at 3500 cm^{-1} becomes small and broadens over time.

At 2950 cm^{-1} , the peak assigned to the C-H bond, the methyl groups react with oxygen forming an oxide compound, presumably on the surface of the preceramic polymer. Furthermore, a large peak is shown in at 1100 cm^{-1} where the Si-O-Si bond is formed. This peak points out that the preceramic polymer undergoes significant hydrolysis at room temperature. Only one day's exposure to a normal atmosphere causes the sample to be hydrolyzed and depolymerized very easily. The hydrolysis for oxidative attack suggests that the properties of the preceramic polymer deteriorate under a high temperature application. Through this experiment, it is identified that the preceramic polymer is susceptible to moisture and the storage method of the preceramic polymer is reliable for the protection from hydrolysis.

Mass curves coupled with TGA oxidation in Figure 4-4 show the difference between hydrolyzed polymer and as-hydrolyzed polymer. Until 400°C , weight loss is not significant. All the samples experienced a significant weight loss at approximately 450°C . At temperatures above 450°C , the hydrolyzed samples exhibit a decrease in the rate of weight, since protective oxide layer on the surface of the hydrolyzed preceramic polymers was formed during air contact. They continue to lose hydrogen, hydrocarbon, and low weight oligomers. However, there are no significant differences in the weight loss behavior of the hydrolyzed samples. The protective oxide layer serves as a diffusion barrier for oxygen. In addition, the interior of the preceramic polymer which is enriched with carbon and boron suppresses cation diffusion. Therefore, the weight loss of the hydrolyzed samples is lower than that of the unhydrolyzed sample.

Although the oxide formation due to hydrolysis gives the decrease in the rate of weight loss, high temperature stability of the preceramic polymers is not directly consistent with the result in TGA measurement. In other words, the TGA does not give information about microstructural changes in the polymer that are associated with weight change. In case of ceramics after pyrolysis of the preceramic polymers, the tendency to the weight loss is rather different from the above TGA result. For the oxygen containing ceramic systems, namely SiCO and SiCNO, the decomposition temperature is slightly decreased compared to the SiBCN systems.¹⁶ If there is oxygen in polysilazane or polyborosilazane, the mechanical performance of the material was found to be greatly decreased compared to oxygen free material. As accompanied by the weight loss, polymer-to-ceramic conversion is necessarily associated with new bond formation. The relationship between heat treatment and structural transformation is discussed using IR and XRD.

4.3 Identification of Preceramic Polymer

4.3.1 Structural Analysis by Infrared Spectroscopy

IR spectroscopy is one of the most powerful spectroscopic tools for the study of polymers. There are a number of reasons for the success of IR. The IR method is rapid and sensitive with sampling techniques that are easy to use. Also, the instrumentation is inexpensive, the operation of the equipment is simple, and service and maintenance of the equipment are not difficult. However, the primary limitation of IR spectroscopy is in quantitative measurements. Although IR measurements are precise about the relative ranking of the amount of specific structures in a set of polymer samples, making accurate absolute quantitative infrared measurements is difficult but necessary. Therefore, IR is usually qualitative or semiquantitative.

4.3.1.1 Bond formation

IR analysis was used to identify the final polymer structure, which may form the expected bonds after synthesis. The FT-IR spectrum of the polymer precursor, shown in Figure 4-5, indicates the formation of various covalent bonds. Asymmetric stretching bands of the N-H and Si-H units are observed at 3393 cm^{-1} , 1176 cm^{-1} and 2156 cm^{-1} respectively.¹⁰⁷ A strong and broad vibration band overlapping with the C-H group appears at 1403 to 1408 cm^{-1} and at 1380 cm^{-1} . These peaks indicate the planar B-N unit characteristic for a pure hexagonal boron nitride.¹⁰¹ The sharp peaks at 2956 cm^{-1} and 2899 cm^{-1} appear separately. These peaks correspond to the formations of the C-H bond and the Si-C bond. Si-C bond stretching absorptions at 1252 cm^{-1} demonstrate the presence of saturated carbons in the chain end group of the structure. A very broad peak at 835 cm^{-1} is due to a Si-N group attached to boron. Finally, a Si-N-Si bond derived from the intermolecular reaction between bulky clusters produces the signal at 940 cm^{-1} .¹⁰⁷ This signal corresponds to that of the absorption of silicon nitride in the crystalline structure. Characteristic band frequencies in the IR region are summarized in Table 4-2.¹⁰⁸

The formation of all bonds in the hypothetical structure is shown by the IR data. The large peaks as a sign of the hydrolysis of the product are not observed in the IR spectra. In case of the hydrolysis of the product, a couple of broad and sharp peaks should be found at around 3500 cm^{-1} and at 1090 cm^{-1} , respectively.^{90,109} More specific short-range sequence can be collected by MAS-NMR analysis. Silicon related characteristic bands that should be found are located in the wavenumber below 1000 cm^{-1} . IR spectrum gives rise to the problem for interpretation of the region due to overlapping of silicon-related bond frequencies with carbon and vibration interferences among the solid samples.

As shown in Table 4-2, most characteristic bands are overlapped so that the interpretation of IR peaks may not give a better scope for identifying the structure.

4.3.1.2 Elimination of byproducts

Internal reflection spectroscopy (IRS) (often called attenuated total reflection or ATR) is a widely used technique for the analysis of polymer samples with low transmission. IRS is a contact sampling method involving a crystal with a high refractive index and low IR absorption in the IR region of interest. The main advantage of IRS is that spectra of opaque samples can be obtained. The obtained solutions of byproducts during polymerization are collected into the flask attached to the end of distillation device at different reaction temperatures. Therefore, in the process of the reaction, the condenser gained low molecular equivalents. It has been reported that elimination of byproducts affects the reaction rate and molecular weight.

As shown in Figure 4-6, the chlorotrimethylsilane peak appears when HMDZ attacks TCS, attaching trimethylsilylamino groups into TCS and eliminating chlorotrimethylsilane from the propagating chains. Its elimination begins around 58 °C. The following elimination comes from the boiling point of hexane solvent at 69 °C. Above 127 °C, unreactive HMDZ, remaining monomers, and HMDZ product among low molecules are eliminated. The IR spectra from the extracts were compared with the spectra of pure material. Consequently, the IR result shows the elimination of byproducts effectively without the use of a vacuum pump at the end of the polycondensation reaction.

4.3.2 Existence of Chlorine by Energy Dispersive Spectroscopy (EDS)

Among the possible challenges is the preparation of large amounts of precursor materials since the byproducts exist often in the form of salts, which must be separated

from the polymeric precursor by a filtration process. Due to the same color, the salt is not distinguishable from the polymer powder during the synthesis process. Any salts are undesirable because they would deteriorate the properties of the preceramic polymer and possibly the ceramic. Besides, the filtration step is both time-intensive and difficult to perform for insoluble polymers. Hence, a special set of bench-top techniques was utilized to develop a system with only volatile byproducts that can be removed by a vacuum and simplify the processing. In order to assure polymerization, the Schlenk technique was introduced to readily eliminate byproducts and prevent hydrolysis.

The EDS analysis shows the existence of the chlorine in the preceramic polymer obtained from the new synthesis method. The pattern (a) of Figure 4-7 comes from the polyorganoborosilazane obtained by the monomer route reported in Riedel et al.⁶ The EDS pattern of individual component effectively determines the distribution and amounts of particular elements on the surface of solid compounds. However, it is not suitable for the determination of the quantity of components with a low atomic number (e.g., B, C or N) or an air-sensitive compound. It was utilized as a qualitative method to identify specific components.

In substance (a), for example, a strong chlorine peak appears at 2.7eV, whereas no chlorine peak appears in the preceramic polymer (b). This difference corresponds to the result obtained from the quantitative potentiometric titration analysis, which shows 4.7 wt% and 100 ppm for the chlorine content of the substance (a) and the preceramic polymer (b), respectively. Therefore, the EDS results identify the elimination of salts, especially ammonium chloride, during synthesis. In addition, the elimination of the salts was successfully achieved by a direct reaction without an additional step.

4.3.3 Structural Analysis by Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) Spectroscopy

NMR spectroscopy is concerned with the detection of absorption or emission of electromagnetic radiation by stimulated transitions between energy levels in the system under investigation. Since the energy levels are influenced by the environment of the nuclei, the resulting spectrum gives direct evidence regarding the chemical nature of interacting atoms, both qualitatively and quantitatively. Spectroscopic data obtained from the chemical shifts and quadrupolar coupling constants of the individual nuclei with each atom surrounded in four different chemical environments provide structural and compositional information of the polymer molecules. However, a dipole-dipole interaction between many interacting nuclei in solids causes the structural interpretation to be difficult, giving rise to the line broadening due to chemical shift anisotropy in polymer orientation.

Fast spinning of a packed polymer powder in rotor inclined to an applied magnetic field removes the chemical shift anisotropy. The magic angle (54.7°) spinning technique provides a narrow line in the spectrum for specific solid samples and shows information on the effects of chain conformation and crystal packing. Thus, the accessible ^{29}Si , ^{13}C , ^{11}B , ^1H and ^{15}N MAS-NMR spectroscopic series could probe the local order of molecular sequence during the structural development of the preceramic polymer.

4.3.3.1 Silicon nuclear magnetic resonance (^{29}Si -NMR)

The ^{29}Si -NMR spectrum of the preceramic polymer (PCP1) in Figure 4-8 is composed of a singlet at 2.0 ppm (Si-C_3) and a singlet at -39.3 ppm (Si-N_3) in a 1:1 integrated ratio. The spectrum of the preceramic polymer indicates the following: (1) two kinds of Si atoms constitute the structure; (2) the atoms are connected to the carbon

(Si-C bond); (3) nitrogen atoms are crosslinked with another Si-containing bulk chain (-Si-N-Si- bond).

4.3.3.2 Carbon nuclear magnetic resonance (^{13}C -NMR)

^{13}C -NMR spectrum is represented in Figure 4-9. The spectrum of the preceramic polymer shows only a strong signal in the aliphatic region. The resonance peak at 3.0 ppm is assigned to the CH_3 group attached to silicon.

4.3.3.3 Boron nuclear magnetic resonance (^{11}B -NMR)

The ^{11}B -NMR spectrum in Figure 4-10 illustrates that only the B-N bond is in the structure. Due to the large quadrupolar moment of the boron nucleus, the ^{11}B -NMR spectrum shows a second-order broadening that cannot be eliminated by fast rotation at the magic angle. The obtained preceramic polymer may have the typical bond structure shown in trigonally coordinated boron nuclei. A local chemical environment of boron atoms in the structure is almost similar to that of the hexagonal boron nitride reported from the ^{11}B -NMR spectrum.²⁶

During synthesis, the formation of B-C bonds has little tendency to connect the boron atom with the CH_3 -site in the hexamethydisilazane molecule instead of the NH-site. From the literature, the ^{11}B isotropic chemical shifts of BN_3 , BN_2C and BC_3 sites are assigned to the values that range from 25 to 30 ppm, 30 to 35 ppm, and 65 to 85 ppm, respectively.¹⁰³ The obtained ^{11}B isotropic chemical shift value of below 30 ppm corresponds to the value reported for the hexagonal BN, e.g., BN_3 sites. It has been known that since B-N domains both serve as diffusion barriers and also inhibit the decomposition reaction at higher temperatures, the presence of the BN domain is related to a prerequisite for the high-temperature stability of Si-B-C-N ceramics.¹¹⁰

4.3.3.4 Proton nuclear magnetic resonance (^1H -NMR)

A representative ^1H -NMR spectrum is observed in Figure 4-11. The effective magnetic field is affected by the orientation of neighboring nuclei. This effect is known as spin-spin coupling, which can cause a splitting of the signal for each type of nucleus into two or more lines. However, the strong ^1H - ^1H dipolar couplings prevent the proton NMR from obtaining a good resolution. For the preceramic polymer, a relatively broad peak appears in ranges from 1 to 5 ppm due to the hydrogen bond in the methyl group attached to the silicon. Peak broadening is very sensitive to the structural complexity. Therefore, the ^1H -NMR spectrum registers various structural units in the amorphous preceramic polymer, which are reflected from the ^{29}Si , ^{13}C and ^{11}B -NMR measurements.

4.3.3.5 Nitrogen nuclear magnetic resonance (^{15}N -NMR)

Some technical difficulties associated with the long spin-lattice relaxation time (T_1) for the low- γ ^{15}N nucleus are present in ^{15}N -NMR. After some manipulations and trials without isotope enrichment of the sample, the weak signals shown in Figure 4-12 can be obtained. It is assumed that the following four types of nitrogen bonds constitute a preceramic polymer: Si-N-Si, HSi-N-B, $\text{Me}_3\text{Si-N-B}$ and B-N-B. A broad spectral component appears in the downfield region at about 78.0 ppm. This peak is attributed to the formation of B-N-B and HSi-N-B units. Overlapping between two bonds was occurred after the formation of crosslinked bonds in the pyrolysis of hydroborated polyhydridovinylsilazane. ^{15}N chemical shifts at 56.0 ppm and 41.0 ppm reported in the literature are attributed to the formation of two kinds of bonds: Si-N-Si and $\text{Me}_3\text{Si-N-B}$, respectively.¹¹¹

4.3.4 Compositional Analysis by Elemental Analysis (EA) and Atomic Absorption Spectroscopy (AA)

4.3.4.1 Elemental analysis (EA)

Figure 4-13 shows the compositional changes of the polymer with increased temperatures. Before pyrolysis, each boron and hydrogen constitutes 7.4 wt% of the preceramic polymer. This amount is higher than the minimum effective hydrogen content of 5% necessary for nuclear field applications.¹¹² It is reported that the final grain size of crystalline phases such as Si_3N_4 and SiC decreases as the boron content of the polymer increases.^{111,113} The higher the boron content in the ceramics, the stronger the influence of the boron bonds on the resulting microstructure. However, much higher boron content in a precursor might not guarantee the dimensional stability of the structure for thermal degradation.¹¹ In effect, the $\text{BN}(\text{C})$ intergranular phase suggests both a decrease of the mobility in the grain boundaries and a suppression of further crystal growth. Boron stabilizes the amorphous state and also increases the temperature of crystallization of thermodynamically stable phases.¹¹⁴ Thus, the phase containing boron is stable at higher temperatures.

As the pyrolysis temperature increases, the carbon/nitrogen ratio decreases due to the more rapid loss of carbon-bearing. In comparison to the silicon, boron, and nitrogen content at room temperature, the loss of carbon content is very high at 1600 °C. A rapid drop of the carbon content up to 800 °C in Figure 4-13 is related with the removal of the carbon at the end of the main chain. The subsequent homolytic cleavage of Si-C bonds removes gaseous products such as methane. The formation of a strong Si-N bond causes a relatively small loss of nitrogen. Until 800 °C, the polyborosilazane preceramic polymer

forms a crosslinking structure with the silicon and nitrogen bond between large molecules by accelerating the dissociation of trimethylsilyl groups stimulated from thermal energy.

The slope of hydrogen content with temperature is relatively steep at 500 °C with respect to other temperature regions. It is due to the evolution of hydrogen gas, leaving the Si-N bond between neighboring molecules. (Figure 4-14) With this kind of reaction, the pyrolyzed precursor has an increase in the content of nitrogen and carbon branched to silicon. The pyrolysis coming from a disordered gas phase reaction among large molecules is completed at the maximum point of 1200 °C. From 1600 °C, the preceramic polymer begins to decompose with the loss of nitrogen. However, it still bears enough nitrogen content at 1600 °C. It has been reported that a number of Si-B-C-N materials show a decomposition temperature between 1600 °C and 1800 °C.^{102,106}

4.3.4.2 Atomic absorption spectroscopy (AA)

Atomic absorption spectroscopy (AA or AAS) is one of the commonly used instrumental methods for analyzing metals and some metalloids. As compared to AA, inductively coupled plasma (ICP) is also a powerful analytical, instrumental method for these elements but at this point its much higher cost limits its widespread use. AA was utilized for the analysis of silicon and boron. The silicon content shows 29.4 wt% at room temperature, but gives an increase of up to 42.9 wt% after pyrolysis at 1600 °C. On the other hand, the boron content decreases from 7.4 wt% to 2.2 wt% after pyrolysis at 1600 °C even though the dissociation energy of B-N bond (110 kcal/mol) is as high as that of the Si-N bond (105 kcal/mol) to maintain its structure at high temperature (Table 4-3).^{115,116}

The change in boron content does not indicate that the absolute value decreases after pyrolysis. In the quaternary SiBCN system, an increase in one component means a relative decrease in the other components. Since the component changes from SiBCNH to SiBCN after pyrolysis, the silicon content increases very much relative to other components. In addition to this result, the compositional change from the initial B:N:Si ratio at 1:2:3 to the final B:N:Si ratio at 1:6:9 is due to the elimination of hydrocarbons as well as the increase in nitrogen crosslinking during pyrolysis. It is also substantiated from the XRD peaks that α - and β -Si₃N₄ exist during the conversion to ceramic at 1600 °C.

4.3.5 Thermal Analysis by Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), and X-ray Diffraction (XRD) Spectroscopy

4.3.5.1 Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)

A TGA analysis of the preceramic polymer shows that the polymer to ceramic conversion occurs in a range from 200 to 800 °C. The polymer to ceramic conversion leads to ceramic yields up to 64% at 1500 °C. The yield of the obtained preceramic polymer in our study is similar to that of HPZ families.¹¹⁷ The initial weight loss observed at 100 to 300 °C could arise through a crosslinking reaction with NH groups in the polymer backbone and Si-N linkages.¹¹⁸ It is noticeable that the formation of a Si-N bond increases as the weight of the polymer slowly decreases near 600 °C. All bond formations and decompositions in the structure are complete up to 800 °C. Further weight loss is not significant at temperatures above 800 °C.

The DSC profile of the preceramic polymer in Figure 4-15 shows a small exothermal event near 300 °C, which correlates with the presence of crosslinking reactions at a lower temperature and the evaporation of typical gaseous products such as

hydrogen, hydrocarbon, amines, and oligomers. Polymers like the HPZ families have a glass transition temperature between 20 °C and 130 °C.¹⁰² It is not clear whether the obtained preceramic polymer shows a T_g around this region. It is common for the preceramic polymer to generate a single endothermic absorption curve usually found in polymers. The large exothermic curves observed near 300 °C and 500 °C indicate the heat required for the molecules to arrange their structure via a new bond formation and crosslinking.

4.3.5.2 X-ray diffraction (XRD) spectroscopy

Figure 4-16 shows the XRD patterns of the preceramic polymers after pyrolysis with different temperatures. The broad featureless diffraction line at all ranges of 2θ , which is typical for amorphous phases, suggests that structural transformation is retarded up to 1600 °C.^{110,117,119,120} The broad peak indicates that the pyrolyzed polymer still keeps its amorphous nature without the formation of a crystalline structure. Above 1600 °C, it can be assumed that the amorphous ceramic starts to undergo crystallization because tiny sharp peaks appear at $2\theta = 28^\circ$, 47° , and 56° . Silicon nitrides (α and β -Si₃N₄) crystalline structures are formed after pyrolysis. This result is consistent with the previous reports of the suppression of crystallization of silicon nitride ceramics by boron nitride.¹²¹⁻¹²³

As shown in Figure 4-13, the results exactly match those from elemental analysis, which has shown the growth for the initial value of silicon and nitrogen in composition compared to the constant value of carbon in composition at 1600 °C. If the polymer has the ceramic structure, it results in thermal stability in opposite to the mechanical degradation. As described before, the conversion to ceramic structure serves as a defect, generating crack origins which are able to deteriorate the mechanical properties. Thus,

the use of amorphous ceramics act as one of advantages for high temperature applications. It is expected that the preceramic polymer in our study will give the same effect.

4.4 Identification of Modified Preceramic Polymers

The polyborosilazane preceramic polymer was modified through two different synthesis approaches. One is to change starting monomers with different side groups. The other is to change the condition of polymerization, such as the reaction molar ratio and the temperature without monomer change for comparison. Through the modification of the reaction variables, how the starting monomer affects the physical and chemical properties of a final ceramic product after pyrolysis is meaningful. Also, the change of the polymerization condition can lead to convert the properties of polyborosilazane preceramic polymer before pyrolysis. To do so, these approaches make it helpful to find an optimum condition in which the products are able to have the best quality.

4.4.1 Evaluation of Modified Preceramic Polymers by Changing Monomers

There are four major factors affecting the speed of a reaction; 1) the properties of reactants and products – in particular, their molecular structure and bonding, 2) the concentrations of the reactants and the products, 3) the temperature at which the reaction occurs, and 4) the presence of a catalysis or its concentration if one is present. The reaction rate can convert the property of a product irreversibly. Control of the reaction rate has been responsible for the quality of product.

In our study, a modification of polyborosilazane preceramic polymer was carried out in order to give polyborosilazane good processability and controlled reactivity by the introduction of a bulkier group into trichlorosilane which has substitutive chlorines. In addition to such a purpose, bulk and reactive side groups make much crosslinking

possible in the structure. For example, a phenyl group has been used for the crosslinking medium between common copolymers in commercially advanced polymer materials, such as PAN (polyacrylonitrile), SBS (styrene-butadiene-styrene copolymer), and so on.

4.4.1.1 Infrared spectroscopy (IR)

The IR spectrum of methyl-substituted PCP2 is very similar to that of PCP1 (Figure 4-17). They show the expected strong and sharp signals for the N-H stretching at 3300 cm^{-1} and 3359 cm^{-1} . Aliphatic C-H vibrations are observed in the 2900 to 3020 cm^{-1} range. The distinct feature of PCP2 is the appearance of Si-H absorption at 2155 cm^{-1} , which peak does not show in the spectrum of PCP1. In contrast to PCP1 and PCP2, IR spectra of PCP3 and PCP4 become more complex as they have bulkier side groups than the former has. PCP3 and PCP4 showed the fast reaction rate during polymerization compared to PCP1 and PCP2. Therefore, it seems that they form a small amount of ammonium chloride due to the peak appearance assigned to NH_4^+Cl at 3156 cm^{-1} . The intensity increases at 1370 cm^{-1} due to a lot of B-N bond formation as compared with PCP1 and PCP2.

In case of PCP4, a sharp peak is shown at 3050 cm^{-1} and 1590 cm^{-1} , which arises from a C=C-H and Ph-Si bond vibration of phenyltrichlorosilane, respectively. The Si-N bond is obtained from the reaction with HMDZ and its peak appears at 1170 , 920 , and 845 cm^{-1} . Since plenty of the carbon and silicon bond are contained initially, Si-C peaks are predominant over all the ranges in the IR spectrum. Compared with Si-N and Si-C, the peak intensity of Si-C at 700 cm^{-1} is a little bit larger than that of Si-N at 845 cm^{-1} . In particular, PCP4 shows much larger increase in peak intensity of 2900 to 3600 cm^{-1} ranges, rather than other preceramic polymers.

4.4.1.2 Elemental analysis (EA)

The result of IR analysis is consistent with the compositional data from EA analysis. Table 4-4 shows that the composition of all the polyborosilazane preceramic polymers at room temperature before pyrolysis. As expected, the carbon content in PCP4 is close to 40 wt%. This value corresponds to the result of the IR spectrum that gives an increase in peak intensity of the Si-C bonds. It is noticeable that PCP1 to PCP3 have a similar value of carbon content, even though the reaction rate of PCP3 was very fast. The reason that the hydrogen content of PCP3 and PCP4 are still low with respect to the value of PCP1 and PCP2 indicates the formation of ammonium chloride as shown in the IR spectra.

The increase in the reaction rate of PCP3 and PCP4 leads to Si-N bond formation resulting in the increase in nitrogen content, 16.3 wt% and 14.2 wt%, from EA analysis. Their values are still larger than PCP1 and PCP2. It is considered that the compositional and structural stability may be kept after the conversion to SiBCN ceramics by pyrolysis. The chlorine content of PCP1 and PCP2 decreases to the level of 100 to 200 ppm as we can observe from the above comparison of EDS pattern. In general, polyborosilazane precursors suffer from the existence of chlorine and the elimination of chlorine with an additional filtering steps.

In our study, the additional filtering step was not utilized for elimination of chlorine. Without the filtering step, the value of chlorine content demonstrates that the synthesis method is reliable for polyborosilazane. As for the final composition of PCP1 and PCP2, the measured ratio of Si:B:N (3:1:1) does not correlate with the hypothesized ratio of 3:1:3 for the structural units Si:B:N in polyborosilazane. Starting from the initial molar ratio did not allow a sufficient substitution of chlorines with the molar ratio of

HMDZ, which is still low enough to replace all chlorines. A desirable nitrogen content can be obtained if the molar ratio of HMDZ increases up to 6 mol or more. Effects on the modification of the molar ratio will be described in the following section.

4.4.1.3 Differential scanning calorimetry (DSC)

Figure 4-18 shows the comparison for the thermal behavior between polyborosilazanes up to 1500 °C. A large trough at the ranges between 1200 °C and 1300 °C indicates that the endothermic reaction takes place in the structure of the polyborosilazane preceramic polymers. To exclude the influence on the sample weight, the same weight of 9.5 mg was utilized in the crucible of the DSC instrument, at the ramp rate 10 °C/min, and under argon atmosphere. It seems that there is a change of flow behavior at two temperature regions of 300 °C and 800 °C. Depolymerization of low carbon-connected molecules or hydrocarbons is related with this heat flow. Large endothermic flow in PCP4 is due to the high carbon content and its decomposition by pyrolysis.

From the minimum point of heat flow in the DSC curve, the amorphous preceramic polymers begin to be crystallized further beyond 1500 °C. Because of the instrumental limit, the thermal behavior of the preceramic polymers was not recorded beyond 1500 °C. This curve does not contain the temperature where polymers convert into ceramics. The behavior of the amorphous preceramic polymers at much higher temperatures can be determined by XRD analysis.

4.4.1.4 Thermogravimetric analysis (TGA)

It has been reported that SiBCN ceramics have weight loss in the range of 30 wt% to 50wt%. TGA studies in Figure 4-19 for polyborosilazane modified samples show a

broad weight loss over the 100 °C to 800 °C temperature range, very similar to the of HPZ families. Clearly, the crosslinking reaction that gives a rapid weight loss for PCP1 at low temperature range has been suppressed in the polyborosilazane modified preceramic polymers. A large weight loss of PCP4 at high temperature is in connection with high carbon content in the composition of the preceramic polymer. The thermal conversion of organometallic polymers into ceramic materials is accompanied by the formation of gaseous byproducts and therefore mass loss during the polymer-to-ceramic conversion. However, the structural change is not directly proportional to weight loss at a relative high temperature in the present polymer system. Low weight loss does not guarantee the conversion to the ceramic at much higher temperatures.

4.4.2 Evaluation of Modified Preceramic Polymers by Changing Reaction Conditions

4.4.2.1 Infrared spectroscopy (IR)

By changing the reaction condition of PCP1, the properties of modified preceramic polymers are identified by IR, EA, TGA, and XRD analysis. The maximum reaction temperature was maintained at 300 °C for 1 h. One of the molar ratios among the starting monomer was modified. The temperature change was not involved with the rate of temperature but with only the maximum temperature at the final stage of polymerization. However, two approaches for modification have a different effect. The temperature change gave only a volume difference of the extracts eliminated by polycondensation. The data obtained from IR and EA analyses does not show the distinct feature between the original and the modified. The reason for the similar result at the different maximum temperatures likely lies in the same reaction rate due to the stepwise increase for the purpose of preventing a radical reaction. The reaction step is summarized in Appendix B.

In an attempt to quantify the difference in a molar ratio of HMDZ, all the conditions remained constant. HMDZ is a function of initiator, which substitutes chlorines and adds its trimethylsilylamino groups. As the reaction proceeds, the intermediate products react with each other forming HMDZ molecules. Nitrogen contained in the HMDZ acts as a crosslinking medium between clusters. Thus, if HMDZ content increases, crosslinked bond increases and finally forms network. It is reported that the preferred ratio of HMDZ per mole of trichlorosilane is between 2.5 to 3 mole.¹²⁴ Thus, thermal stability can be predicted by the increase in Si-N bond which HMDZ possesses.

During polymerization, plenty of HMDZs react with borontrichloride and trichlorosilane abruptly forming N-B bonds and Si-N bonds at a initial stage. This reaction essentially effects the rate of crosslinkage. After reaction, the product was polymerized in the form of a translucent gel. In general, gelation is conversion of a liquid to a gel state. A dramatic increase in viscosity occurs due to initial network formation. At this reaction, gelation does not mean the simultaneous hydrolysis and polymerization reaction. Such a polymerization was tried 3 times. All the products were gained in the form of gel. Even though the maximum reaction temperature was increased up to 300 °C in order to change the present phase into the solid phase, no powder was produced.

Figure 4-20 shows the increase in peak intensity at 1350 cm^{-1} and 800 cm^{-1} assigned to B-N and Si-N, respectively. The characteristic band positions exactly coincide with each other. However, the peak intensity is found to be evidently different. As a general rule, IR peak intensity is increased when the vibrating and stretching atoms have significantly different masses. The IR spectra result from the increase in the number

of bond formation. Therefore, it is evident that the change in the molar ratio of HMDZ accelerates the bond formation related to the crosslinking reaction. The IR result corresponds to the EA result for compositional change.

4.4.2.2 Elemental analysis (EA)

The increase in the molar ratio of HMDZ gave rise to a large increase in carbon and nitrogen content. The increase in nitrogen content was particularly predominant in the structure. As shown in Figure 4-21, it seems that an initial gelation stimulated by the formation of nitrogen bond prevents a late crosslinking which provides a slight increase in nitrogen content at 200 °C for PCP1 at 1:1:4. At 1000 °C, the increase in nitrogen content exceeds the increase in carbon content caused by a large increase in the number of Si-N and B-N bonds in comparison with other bonds. It suggests that the modified preceramic polymer should have thermal resistance to the structural transformation at high temperatures. Moreover, the modified preceramic polymer keeps nitrogen content constant up to 1600 °C.

Similar to the weight loss curve for PCP1 to PCP4 in the TGA analysis, the curve in Figure 4-22 shows that PCP1 at 1:1:6 as well as modified preceramic polymers (PCP2, PCP3 and PCP4), which may have the structural stability under a thermal condition is not in accordance with the resistance to weight loss at a relative low temperature range. The weight loss for PCP1 at 1:1:6 is inferior to that for PCP1 at 1:1:4. It is not evident that the thermal stability of polymers is strongly connected with that of ceramics in our study.

Despite a slight difference in weight loss for PCP1 at 1:1:6 relative to PCP1 at 1:1:4, the XRD peaks (Figure 4-23) of those materials show a big difference on the structural transformation. Pyrolysis was carried out at 1600 °C for 12 h holding time. In

spite of the sharp peaks for the original, the modified preceramic polymer shows no crystalline peaks. This could account for the variable carbon and nitrogen content of different samples. The modified preceramic polymer has high nitrogen content (22.5 wt%) at 1600 °C. Bond cleavage by pyrolysis was not considerable for a long time exposure. This phenomenon is not related with the fact that the preceramic polymer lost a large amount of its weight during pyrolysis at low temperatures. It is likely to depend on the bond strength and the amount of nitrogen in connection with silicon and boron after the conversion to amorphous ceramic. Therefore, it can be possible for the preceramic polymer in gel state to be utilized by fiber spinning.

4.5 Identification of Pyrolyzed Preceramic Polymers

The precursors produced above are transformed into ceramics by pyrolysis in inert gas atmospheres. This polymer-to-ceramic conversion is accompanied by the formation of gaseous species during pyrolysis. Polyborosilazane preceramic polymers were converted into SiBCN-containing ceramics at high temperatures. In the course of the pyrolysis, polyborosilazanes change their structure and composition with a different mechanism. Their changing mechanisms are not well revealed because thermal reaction is very sensitive to environmental changes and the sample handling, as well as a lack of the instrumental versatility. Many research groups have been searching for the accurate mechanism to assess the polymer-to-ceramic conversion by spectroscopes and thermal analyses. A more fundamental analysis of the conversion phenomena in our study is presented.

4.5.1 Infrared Spectroscopy with Different Pyrolysis Temperatures

With increasing temperature, the structural changes of the pyrolyzed polymer were examined. A stepwise loss of functional groups was revealed by an infrared study on the ceramic conversion process of the preceramic polymer.^{102,125,126} Figure 4-24 shows that the peak intensity of the N-H bond begins to decrease relative to the Si-H and C-H absorptions at 200 °C. Furthermore, the N-H peak decreases at 400 °C. However, both Si-H and C-H absorption peaks nearly disappears at 500 °C. Peak broadening at 800 °C becomes evident near 3500 cm⁻¹. Similar results are shown in an infrared study on the pyrolysis of hydridopolysilazane polymers.¹⁰³ Bulk pyrolysis of the preceramic polymer above 1000 °C gives low ceramic yields: 72%, 62%, and 53% at 1000 °C, 1400 °C, and 1600 °C, respectively. The hydrogen bonds disappear above 1400 °C. At higher temperatures, a Si-N bond appears as a result of the elimination of a B-N bond in the main backbone with a portion of hexamethyldisilazane. Consequently, it is supposed that the transition phenomenon from an amorphous structure to a crystalline structure having Si-C, B-N, and Si-N as main bonds begins at temperatures above 1600 °C.

Contrary to the most marked interaction at 2100 cm⁻¹ in the previous figure, the IR peak for PCP2 having methyl group disappears (Figure 4-25). A big change comes from 800 °C. The appearance of a peak at 1000 cm⁻¹ is due to a Si-CH₂-Si bond which was formed by the reaction with neighboring molecules and methyl group in methyltrichlorosilane. The peak was maintained at 1000 °C. As shown in Figure 4-12, carbon content did not decrease because such a bond still remains at 1000 °C without

decomposition. It is evident that the weight loss and structural transformation can be retarded due to the peak existence of B-N and Si-N at 1600 °C.

Due to the complexity of the chemical structure and the extensive coupling of vibrating motion, IR spectra for PCP4 makes the interpretation difficult (Figure 4-26). The peak at 933 cm^{-1} is assigned to the $\text{Si-CH}_2\text{-CH=CH}_2$ bond which is generated from the cleavage of the phenyl group in phenyltrichlorosilane. This peak becomes weak and disappears at 500 °C. On the other hand, the intensity for N-H bending becomes much larger at 800 °C indicating that the crosslinking reaction proceeds further. In particular, the linkage between the phenyl group and the silicon backbone chains was represented at 1135 cm^{-1} . Specific Si-phenyl compounds often can be identified by the peaks at 1589, 1115, and 736 cm^{-1} . At 800 °C, their peaks disappear and therefore large weight loss is shown in the TGA curve. Also, the intensity of the Si-NH-Si bond becomes lower at that temperature. SiCl_2 and SiCl_3 compounds represent two bands in the low wavenumber range. It indicates that the elimination of ammonium chloride was not sufficiently eliminated during polymerization.

4.5.2 Elemental Analysis with Different Pyrolysis Temperatures

The evolution of carbon and nitrogen content for PCP2 is similar to that of PCP1. The result is due to the starting material of PCP2 analogous to that of PCP1 (Figure 4-27). The use of methyltrichlorosilane did not produce a significant change in the composition of the preceramic polymer and nor in thermal behavior. At 800 °C, the increase in nitrogen content was accompanied by not so much as the bond formation but by the decomposition of carbon. The nitrogen bond formation is extended into rather a higher temperature, since a number of nitrogen bonds are formed during polymerization.

The monomer structure of a larger side group makes a space in the molecules, which makes it possible for the addition into many short chains. As described above, the result similar to PCP1 was shown in TGA and DSC curves.

Elemental studies further support a silazane backbone constituent for PCP4 (Figure 4-28). The considerable increase arises from the use of the phenyl group, resulting in the large initial value in the carbon content. By 1600 °C, the drop of carbon and nitrogen content is not significant. As for the carbon and nitrogen content at 1000 °C, the increase is as good as large. It is possible to identify the structural stability of PCP4 with high carbon and nitrogen content up to 1600 °C by XRD analysis.

Table 4-5 represents the weight losses of polyborosilazanes at different temperatures and holding times. In the case of PCP1 and PCP2, the weight loss becomes more serious at 1000 °C in contrast to the case of PCP3 and PCP4, which undergo the large weight loss from 800 °C. This phenomenon shows that PCP3 and PCP4 have a more complex structure from the starting monomers and have stronger bonds from weight loss. The remaining bonds turn out to be stable compositionally and structurally. Therefore, at much higher temperatures, weight loss changes eventually decrease. Even to extended holding times, the increase of weight loss for PCP3 and PCP4 has a half value compared to the value of PCP1 and PCP2.

The final weight losses of the samples pyrolyzed at 1600 °C for 12 h show the opposite result to the data from TGA analysis. It is interesting to note that among the samples, PCP3 has the lowest value in weight loss. Even though all the samples increase in their weight loss under thermal exposure for a longer holding time, PCP3 is expected to have the excellent thermal stability in XRD analysis.

4.5.3 Thermogravimetric Analysis and Differential Scanning Calorimetry with Different Pyrolysis Temperatures

Our study is focused on the identification of the thermal behavior in ceramics obtained from pyrolysis of the polyborosilazane preceramic polymers. The same weight of the preceramic polymers was pyrolyzed at each temperature for 1 h holding time. The thermal analysis was performed by DSC and TGA with ceramics obtained from the pyrolysis of the polyborosilazane preceramic polymers. All the samples until 800 °C still contain a small amount of hydrogen, 1 wt% to 2 wt%. As shown in Figure 4-29 and Figure 4-30, pyrolyzed ceramic at 500 °C represents initial weight loss due to a large crosslinking reaction around 700 °C. This loss arises from the relatively large hydrogen content (5 wt%) after pyrolysis at 500 °C, which is readily eliminated by thermal decomposition. Also, the sample is under an initial crystallization reaction at 900 °C owing to the appearance of the exothermic curve.

The lowest curve in the TGA is from the polyborosilazane preceramic polymer without pyrolysis. The weight loss has a very large value of 38% compared with others. The pyrolyzed ceramic at 800 °C gives a rapid weight loss at 200 °C, but subsequently does not show a large change in the weight loss. It is considered that the influence of a sudden drop of carbon content at initial stage is compensated by the increase in nitrogen bonds. The pyrolyzed ceramic at 1000 °C shows only slight decrease in the weight by 1500 °C. In the contrary, the weight loss stays constant for the pyrolyzed ceramic at 1400 °C. Therefore, it is recommended that SiBCN ceramics should be fabricated at least above 1000 °C for high temperature applications.

4.5.4 X-ray Diffraction Spectroscopy with Temperatures and Holding Times

4.5.4.1 Oxygen content in the furnace

The resistance to oxidation of SiBCN ceramics has been of interest from over the past 20 years. It is difficult to compare results from one study to another, since there are a number of variables that will effect an oxidation result, for example, composition of SiBCN, the pyrolysis temperature employed to make SiBCN, the oxidation temperature, the form in which the SiBCN is oxidized, and the furnace conditions. Thus, the difference depends how the result or extent of the oxidation is assessed.

All of the preceramic polymer pyrolyses were carried out in a Lindberg Model tube furnace fitted with a temperature controller. The pyrolysis was conducted under high purity argon gas at a $200 \text{ cm}^3/\text{min}$ purge rate sufficient to prevent decomposition and redeposition of the vapors that were evolved during the pyrolyses. The samples were transferred to the pyrolysis tube which was then sealed from the atmosphere and flushed with argon.

Before pyrolysis, oxygen content in the tube furnace was measured by an oxygen analyzer and recorded with elapsed time. From a 99.99% pure argon gas cylinder to the inlet of the furnace, the furnace initially gained 26 ppm in the original oxygen content due to a small portion of oxygen penetration into the gas line. During 3 h, O_2 content was monitored by an oxygen analyzer attached to the outlet of the furnace. The recorded oxygen contents with time are shown in Figure 4-31. After 3 h, the furnace contained 6 ppm O_2 . This value is enough to bring about the oxidation between the substance. To reduce the oxygen content in the furnace, the furnace was perfectly sealed. Flow rate of argon gas was doubled. Before pyrolysis, the furnace containing sample was flushed with

argon for 24 h. It is expected that with a long time purging, the pyrolysis of the sample guarantees the reliability for the oxidation protection.

4.5.4.2 Comparison at the same temperature

SiBCN ceramics have been utilized as a high temperature material. They have an amorphous structure strongly influenced by the structural feature of a boron and nitrogen molecule. When the temperature increases, the amorphous polymers convert their structure into crystalline. Boron can retard its temperature toward a further higher temperature. The existence of the crystalline structure causes crack origin in the structure of the materials. Therefore, it has been required to develop the material without any structural transformation at a high temperatures.

Figure 4-32 shows the comparable results obtained from the pyrolysed preceramic polymers at 1600°C for 1h holding time. Each of them have a different degree of crystallinity at the temperature. The degree of crystallinity corresponds to the intensity and the number of sharp peaks. Compared with PCP2 and PCP3, PCP1 shows a rather sharp peak and three tiny peaks. It is not well regarded that PCP1 has plenty of crystalline in the structure. Only the large peak at 28° shows the existence of a Si_3N_4 crystalline structure. Except for the peak at 28°, the other peaks are not distinguishable whether they are peak or noise. Therefore, PCP1 starts conversion of its structure at 1600°C.

Modified preceramic polymers (PCP2 to PCP4) give a better result. Since an introduction of bulky side groups to the polymer structure hinders the arrangement of the molecules and offers much more content (C, N, and Si) to the constituents, the thermal behavior can be changed for a better result. The self-diffusion coefficients of nitrogen and carbon decrease with increasing boron content, while that of silicon is decreased by

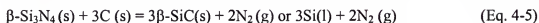
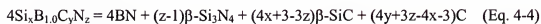
increased amounts of carbon.¹²⁷ Decreased atomic diffusivities of the constituent elements silicon, carbon, and nitrogen correspond to enhanced thermal stability of amorphous SiBCN preceramic polymers.

The study of the effect on the increase in the pyrolysis temperature beyond 1600 °C is restricted by the maximum furnace temperature. However, it is possible for the equivalent effect on the increase in the pyrolysis temperature to be attained by the increase in holding time.

4.5.4.3 Comparison at different holding times

The increase in a holding time was intended to influence the increase in pyrolysis temperature. Figure 4-33 illustrates that the change in the XRD pattern with respect to different holding times at 1600 °C is verified. Peak intensity is changed with the holding times. For a holding time of 12 h, PCP1 forms the crystalline structure at all angle ranges. This means that the amorphous PCP1 transforms into the crystalline ceramic, such as α -Si₃N₄, β -Si₃N₄, β -SiC and elemental Si. Initial crystallization of β -SiC is usually observed for 12 h.

All the SiBCN materials known so far contain excess carbon with respect to their thermomechanically stable binary phases, namely SiC, BN, and Si₃N₄.^{17,78,120,128} Thus, the crystallization and subsequent decomposition of SiBCN materials at $T > 1450$ °C and under 0.1 MPa nitrogen pressure follows Equation 4-4 and 4-5,^{6,129}



Accordingly, Si_3N_4 formed by crystallization of the amorphous SiBCN network is expected to react with excess carbon to form SiC and elemental nitrogen gas. The low carbon contents of the ceramics and the inclusion of boron into the ceramic lead to the conversion of $\alpha\text{-Si}_3\text{N}_4$ to $\beta\text{-Si}_3\text{N}_4$. As pure boron nitride would be expected to have crystallized by 1800 °C, the absence of BN diffraction in the XRD of the PCP1 is consistent with the above result.

In the case of PCP2 (Figure 4-34), the crystallization for 1 h at 1600 °C is not shown. Even the pyrolysis for 6 h and 12 h does not give a lot of sharp peaks. It becomes clear that $\alpha\text{-Si}_3\text{N}_4$ and $\beta\text{-SiC}$ crystalline ceramics have been growing with long holding times. However, the elemental Si crystalline structure is not yet present for all holding times. PCP2 is more stable than PCP1, judging from the sharp peak intensity and number.

PCP3 does not show structural change after 12 h pyrolysis. As shown in Table 4-4, the weight loss for PCP3 is relatively lower than others. The data results in the fact that the boron and nitrogen content is maintained for a longer time at higher temperatures. PCP3 has still significant retention of nitrogen with the XRD peaks showing the only tiny presence of $\beta\text{-Si}_3\text{N}_4$ at 1600 °C for 12 h holding time (Figure 4-35). It means that the PCP3 ceramic is still amorphous at 1600 °C for all holding times.

It is known from the literature that hydrogen attached to silicon increases the thermal stability of SiPh units.¹³⁰ The SiPh units allow PCP4 to have high carbon content and steric hindrance. However, the effect is not much higher with respect to the structure. Si-Ph units were not present up to 1000 °C, as shown in Figure 4-26. However, the increase in carbon content was still considerable at 1600 °C for 1 h holding time. This allows PCP4 to form $\beta\text{-SiC}$ crystalline ceramic. For a longer holding time, PCP4 begins

to decompose with loss of nitrogen and both α -Si₃N₄ and β -Si₃N₄ crystallize (Figure 4-36). Studies of the PCP modified ceramics, as well as other SiBCN systems, have demonstrated that as little as 2wt% boron inhibit their decomposition and change their crystallization behavior.^{76,131-137}

Pyrolyses carried out to longer holding time at 1600°C demonstrate higher ceramic yield for PCP3 compared to other samples. As shown in Figure 4-37 and 4-38, the elemental analyses also show much longer retention of nitrogen and carbon at high temperatures for PCP3 compared to others. While PCP1 and PCP2 contain only 3.0% nitrogen for 12 h holding time, PCP3 contains 13.5% nitrogen for 12 h holding time. In addition, the slope of nitrogen content in PCP4 dramatically decreases with longer holding time. On the contrary, the slope of nitrogen content in PCP3 is maintained without large decrease. This phenomenon is relatively insignificant in the carbon content except for PCP4 which has very large carbon content. Thus, one of the polyborosilazane preceramic polymers derived from structural modification is compositionally more stable at a temperature to which the other samples normally evolve nitrogen.

Different patterns of the onset, the phases, and the extent of crystallization are observed from the pyrolyzed ceramics obtained by the modification. As shown Figure 4-31, the modified polyborosilazane preceramic polymers (PCP2, PCP3, and PCP4) do not clearly show any major crystallinity at 1600°C, at which temperature a mixture of α -Si₃N₄ and β -Si₃N₄ is observed. However, it becomes clear that with increased holding time, the ceramic forms the crystal structure.

4.6 Application to the Nuclear Field

In the last decade there have been a number of materials that have shown promise for enabling the production of a homogenous polymer with SiBCN components for high temperature and nuclear applications. However, the synthesis of these compounds tends to involve too many steps, and are too complex, and come at a high cost. A new method was developed for forming SiBCN-based polymers to be used as BPRAs in nuclear reactors or in other extreme temperature conditions that will save energy companies and launch equipment manufacturers significant time and money.¹³⁸ Therefore, our research is seeking a technology to commercialize a novel process for forming preceramic polymers to be used as materials in burnable poison rod assemblies and/or spent fuel containers.

A BPRA is a bundle of rods inserted into a nuclear reactor core during refueling to control radioactivity levels inside the reactor. However, currently used polymers for BPRAs contain boron carbide (B_4C) in an alumina matrix (Al_2O_3), which are chemicals that do not completely burn off the radioactive poison at the end of the reactor cycle. Although it has been known for more than a decade that using SiBCN polymers would leave virtually no residual poison, they are very costly and difficult to synthesize. This section verifies how much SiBCN preceramic polymers are hydrothermally stable under the high-temperature conditions similar to a nuclear reactor.

4.6.1 Autoclave Test

In order to assure the potential of the preceramic polymer in nuclear applications, where a hydrothermal condition can exist through the failure of zircaloy cladding, autoclave testing was performed under conditions similar to the nuclear environment at 350°C and 3000 psi for 24 h in water. The preceramic polymer powder was fabricated in

the form of a pellet to insert the powder into the holder of the autoclave. This step gave poor processability, even though the pellet was made into a disc under pressure without heating. Both the high molecular weight and low population of pendant groups and side chains in the preceramic polymer, as a result of the full substitution, probably contributes to the poor processability of the pellet. Before test, deionized water in the autoclave was taken as a reference for inductively coupled plasma (ICP) analysis. After completion of the test, the water condensed by vaporization during test was collected into the holder vessel of the autoclave.

4.6.2 Characterization

After the autoclave test, the boron content of the effluent from a dissolved polymer pellet in water was analyzed by ICP. The autoclave data is summarized in Table 4-6. The boron content of the effluent from a dissolved polymer pellet in water dropped below 200 ppm, which is an extremely low amount compared to the boron content of other carborane polymers prepared under different synthesis methods. The results demonstrate that a silazane polymer containing boron may remain stable under hydrothermal environment of a nuclear reactor.

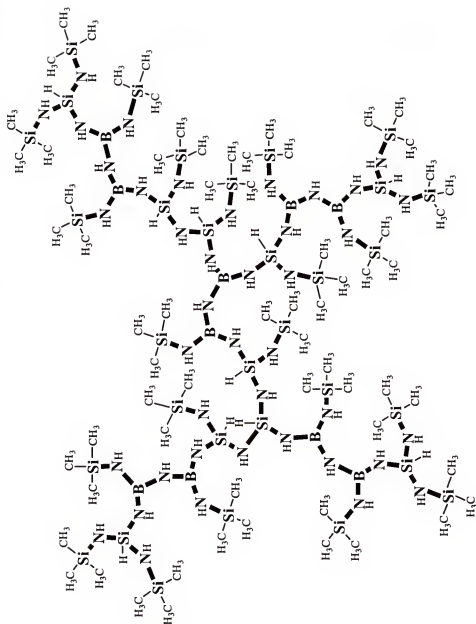


Figure 4-1. Proposed final structure of polyborosilazane preceramic polymer

Table 4-1. Yields of polyborosilazane preceramic polymers after various synthesis routes

Product	PCP1		PCP2	PCP3	PCP4
Monomer	HSiCl ₃	HSiCl ₃	CH ₃ SiCl ₃	C ₂ H ₅ SiCl ₃	C ₆ H ₅ SiCl ₃
Molar ratio	1:1:4	1:1:6	1:1:4	1:1:4	1:1:4
Trial	10	3	3	1	1
Total feeding weight (g)	46.2	37.5	46.8	47.1	48.8
Final gain (avg.) (g)	3.6	2.2	4.5	3.0	5.6
Phase	Powder	Gel	Powder	Powder	Powder
Yield (%)	85.4	85.8	87.2	87.5	91.2

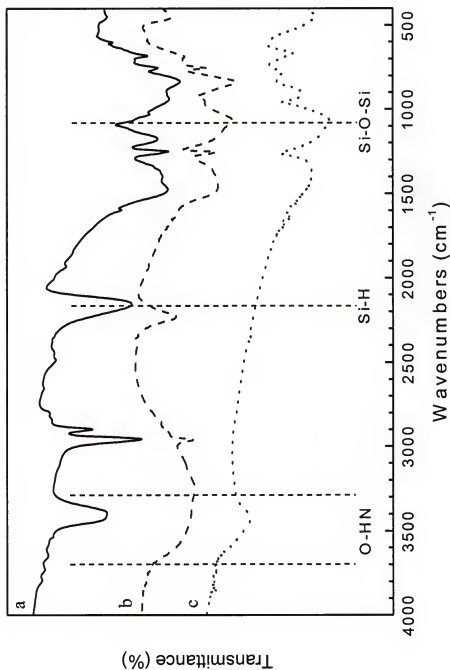


Figure 4-2. IR spectra on the hydrolysis of the preceramic polymer in air contact
(a) preceramic polymer (b) 3 days exposure in normal atmosphere, and (c) 1000 $^{\circ}\text{C}$ in air

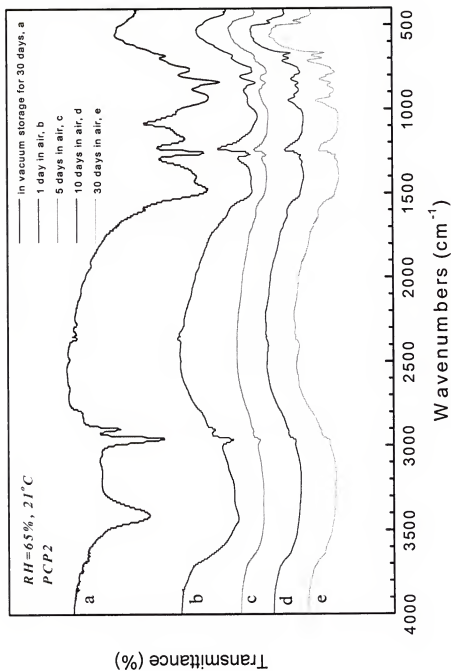


Figure 4-3. The hydrolysis of polyborosilazane in different storage state

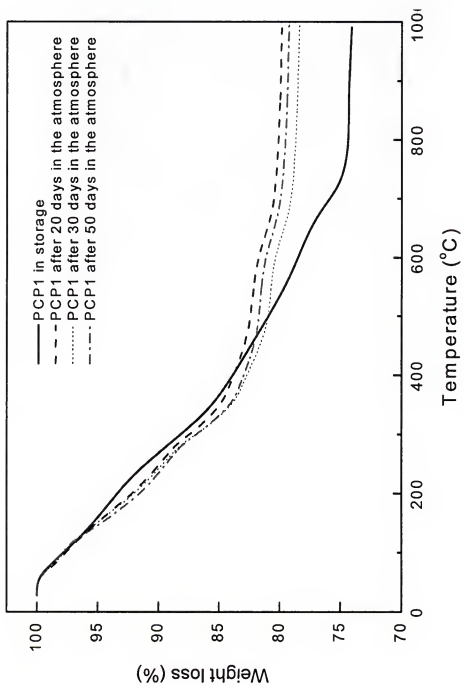


Figure 4-4. Comparison of hydrolyzed polyborosilazanes by way of weight loss

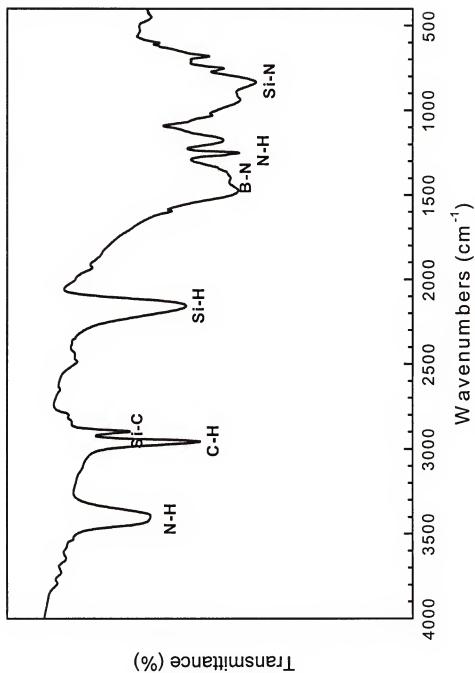


Figure 4-5. FT-IR spectrum of the preceramic polymer illustrating bond formation

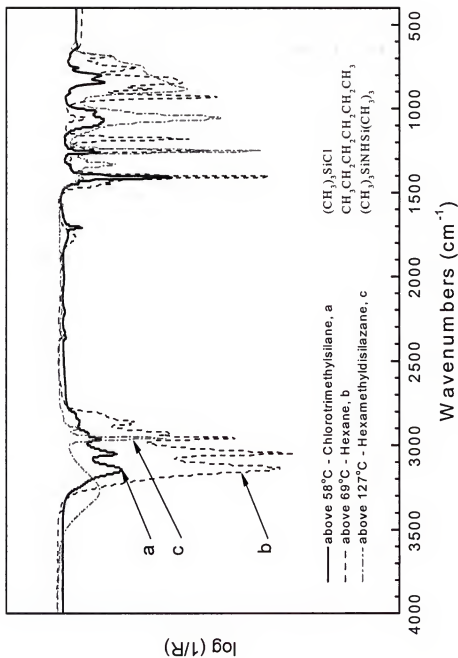


Figure 4-6. IR spectrum of the preceramic polymer illustrating elimination of byproducts

Table 4-2. Characteristic band frequencies in IR region

Bonding groups	Characteristic band frequencies (cm ⁻¹)
C-H	2700-3300 (stretch), 1300-1470 (bend), 600-900 (rock), 2950, 2895, 2800
C-CH ₃	2850-3010(s), 1440-1490(s), 1350-1400(m)
CH ₂ -O-CH ₂	1050-1180(s)
O-H	3030-3700 (stretch), 1200-1450 (bend)
Si-O	1100-1120
Si-OH	3690 (free OH), 3400-3200 (hydrogen bonded OH), 950-810
Si-O-Si	1130-1000
Si-CH ₃	1230-1280(s), 1275, 800-825
Si-CH=CH ₂	1600, 1410, 1010, 960
Si-CH ₂ -CH=CH ₂	1640-1630, 1190-1140, 990, 930
Si-C ₆ H ₅	1600-1590, 1430, 1130-1110, 1030, 1000, 760-710, 700-690
Si-Ph-Si	1135
Si-C	700-860(w)
Si-H	2100, 2145
Si-NH-Si	1180, 915
Si-Cl	625-425
Si ₃ N ₄	840 (Amorphous silicon nitride has a strong, broad absorption band)
SiC	800 (All forms of SiC will show strong absorption band)
N-H	1500-1650 (bend), 3400, 1200
NH ₄ ⁺ Cl	3050-3150(m), 1370-1430(m)
Planar B-N units	1248
B-N	1350-1370, 1460 (stretch)
Pure hexagonal B ₃ N ₄	1347
C-N	1390
B-C	1275-1425, 1300

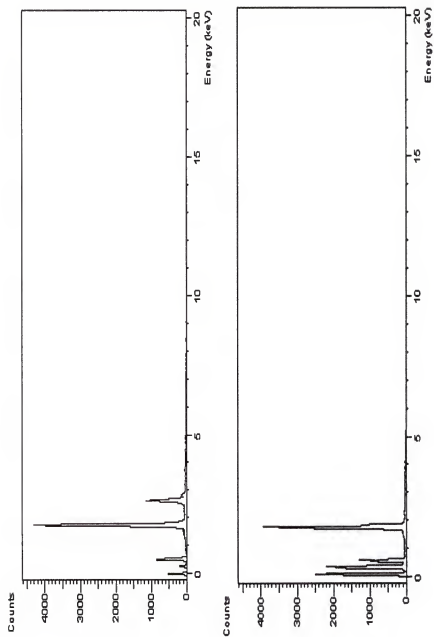


Figure 4-7. EDS spectra of two different types of preceramic polymers (a) Cl-containing polyorganoborosilazane and (b) polyborosilazane

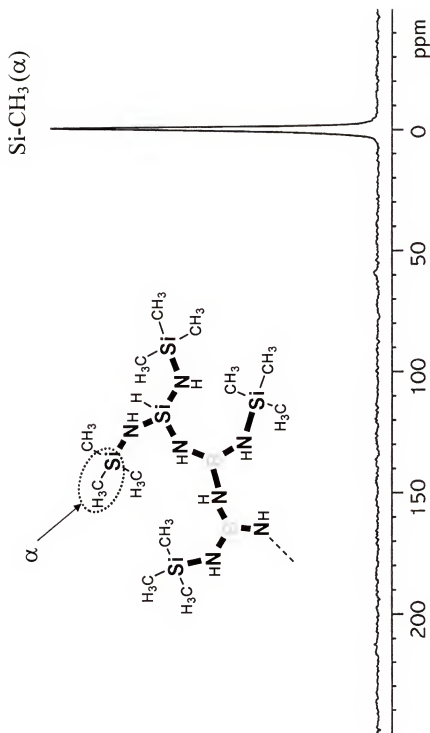


Figure 4-9. ^{13}C -NMR spectra of the preceramic polymer (PCP1)

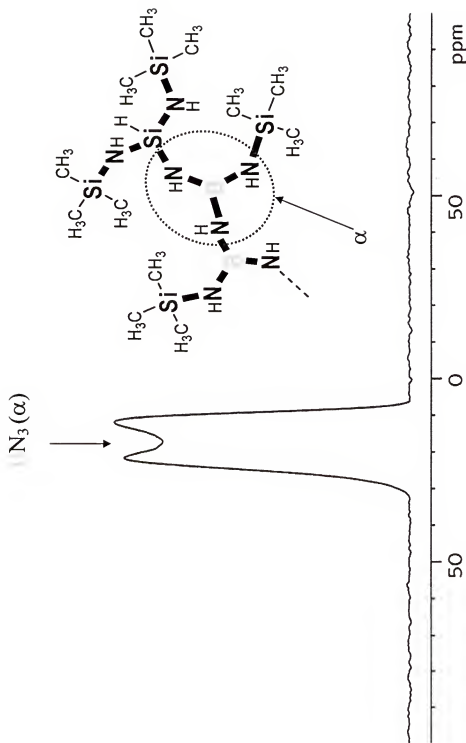
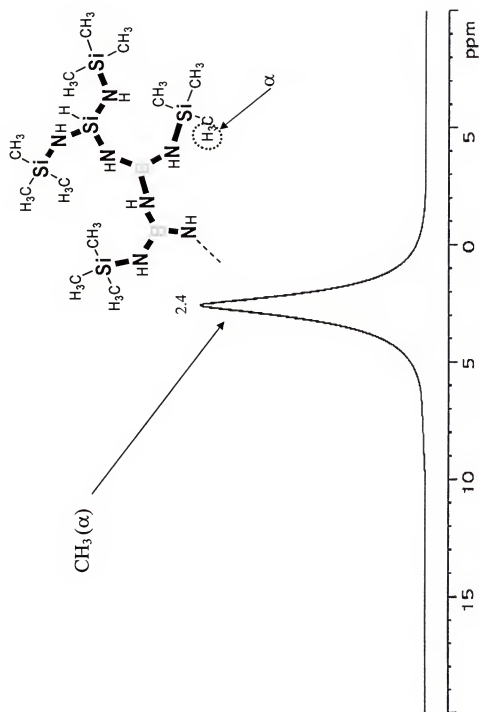


Figure 4-10. ^{11}B -NMR spectra of the preceramic polymer (PCP1)

Figure 4-11. $^1\text{H-NMR}$ spectra of the preceramic polymer (PCP1)

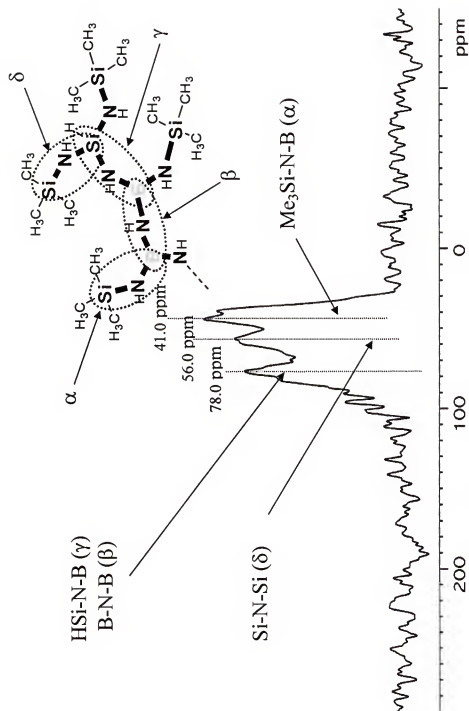


Figure 4-12. ^{15}N -NMR spectra of the preceramic polymer (PCP1)

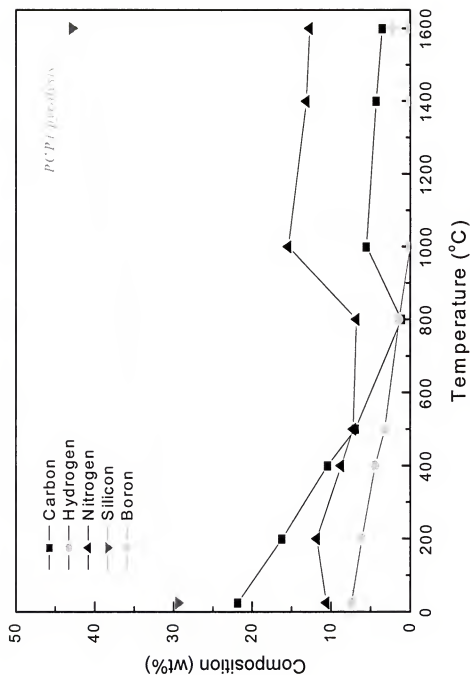


Figure 4-13. Compositional change of the preceramic polymer at different pyrolysis temperatures under argon atmosphere

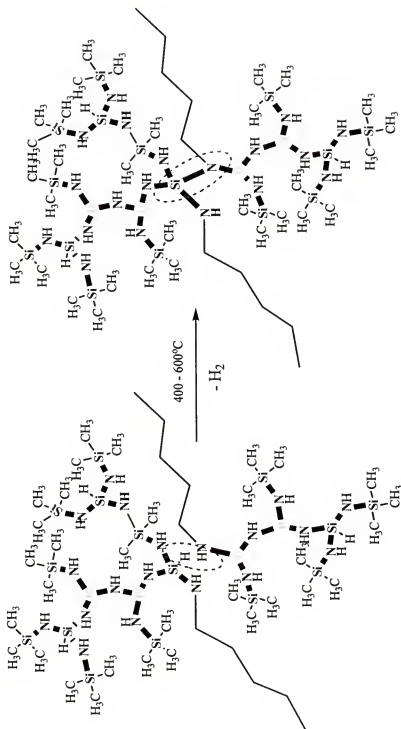


Figure 4-14. Evolution of hydrogen gas during pyrolysis

Table 4-3. General magnitude of bonds

Bond	Dissociation energy (Kcal/mol)	Bond	Dissociation energy (Kcal/mol)
B-N	110	Me ₃ Si [•]	3 - 5
B-C	89	C ₆ H ₅ SiH ₂	65
C-C	83	MeSi [•] H	50
C-H	99	H ₂ C-H	110
C-N	75	SiCl ₃ [•]	79
C-O	85	Me ₃ Si-Cl	114
H-H	104	Me ₃ Si-NHMe	100
Si-H	70	Me ₃ Si-N(SiMe ₃) ₂	108
Si-Si	55	CH ₃ NH ₂	96
Si-C	75	SiCl ₃ -H	95
Si-N	105	Me ₃ Si-SiMe ₃	80
Si-O	110	Me ₃ SiH-CH ₃	94
N-N	41	Me ₃ Si-CH ₃	91

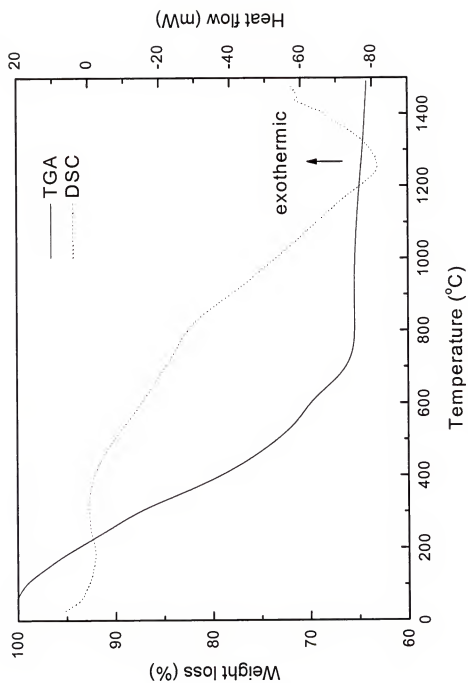


Figure 4-15. TGA/DSC curves for weight loss and heat flow of the preceramic polymer

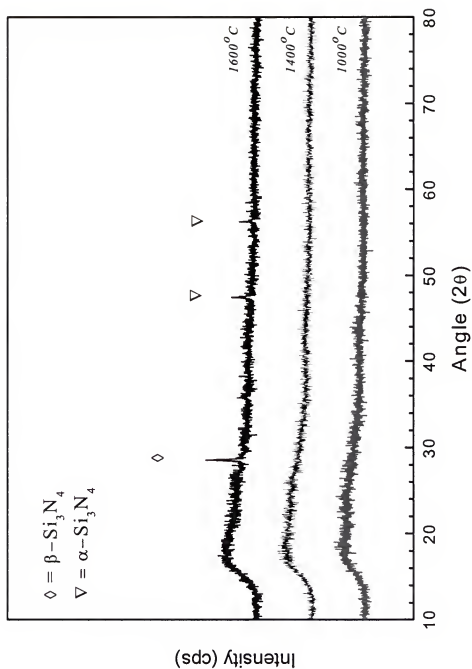


Figure 4-16. XRD patterns of the preceramic polymer after pyrolysis at various temperatures

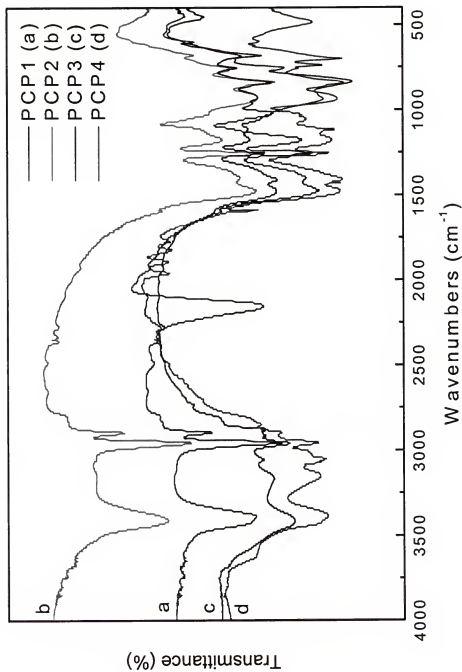


Figure 4-17. IR spectra of different types of polyborosilazanes

Table 4-4. Composition of preceramic polymers at room temperature measured by elemental analyzer, atomic absorption spectroscopy, and potentiometric titration

Polymer	Carbon (C)	Hydrogen (H)	Nitrogen (N)	Silicon (Si)	Boron (B)	Chlorine (Cl)
PCP1	21.8	7.4	10.6	29.4	7.4	0.01
PCP1116	24.9	6.3	22.2	-	-	-
PCP2	20.9	7.6	12.8	31.1	8.0	0.02
PCP3	23.5	6.3	16.3	-	-	-
PCP4	39.5	5.8	14.2	-	-	-

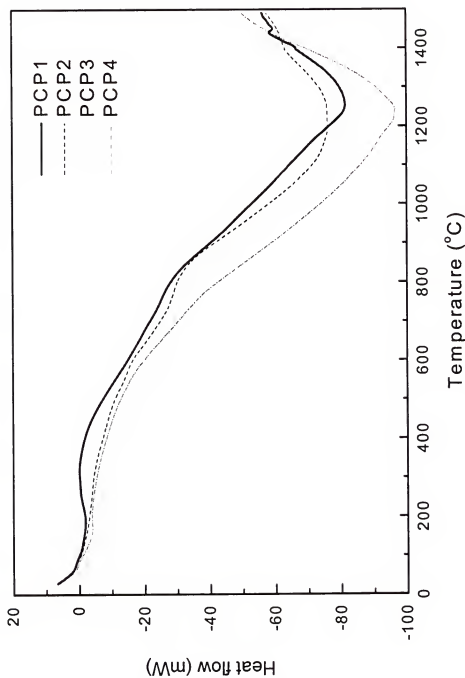


Figure 4-18. Comparison of polyborosilazanes thermal behaviors by differential scanning calorimetry

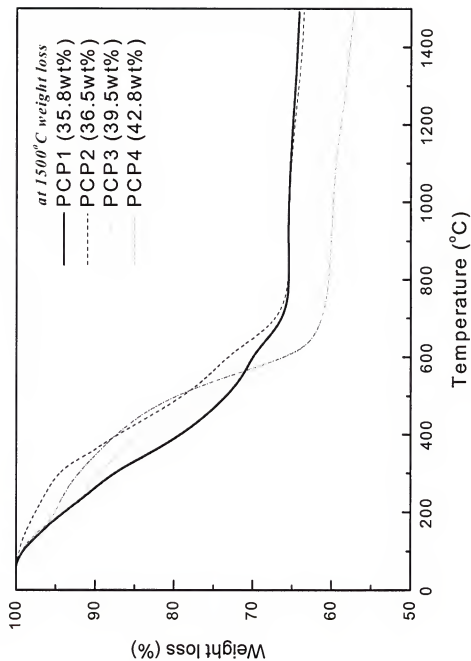


Figure 4-19. Comparison of polyborosilazanes weight loss by thermogravimetric analysis

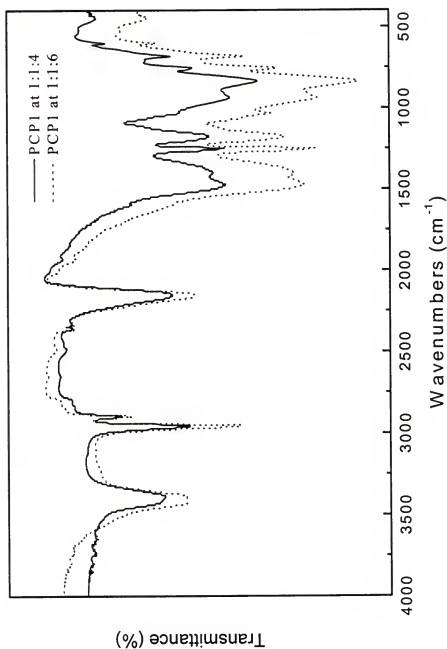


Figure 4-20. IR spectra of polyborosilazanes at different molar ratios

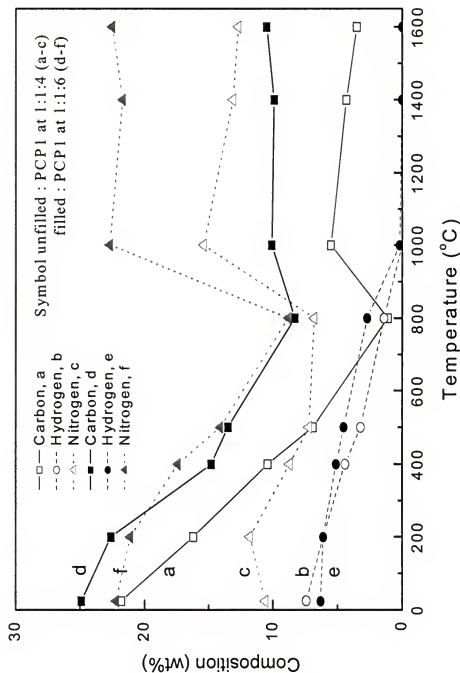


Figure 4-21. Compositional change of the preceramic polymer at different molar ratios

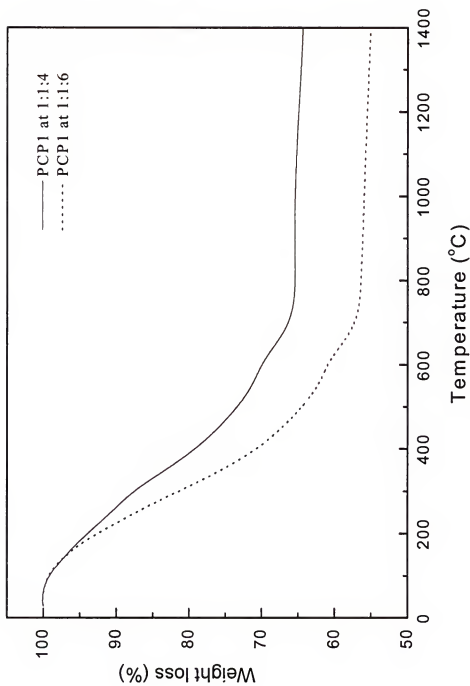


Figure 4-22. Comparison of polyborosilazanes at different molar ratios with weight loss in TGA

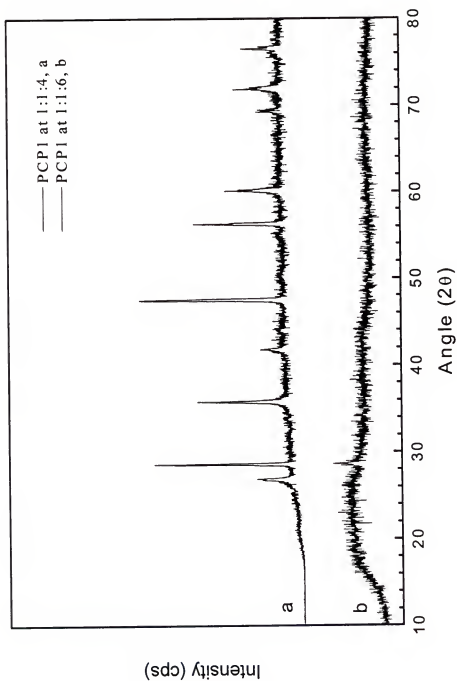


Figure 4-23. XRD patterns of polyborosilazane (PCPI) at different molar ratios

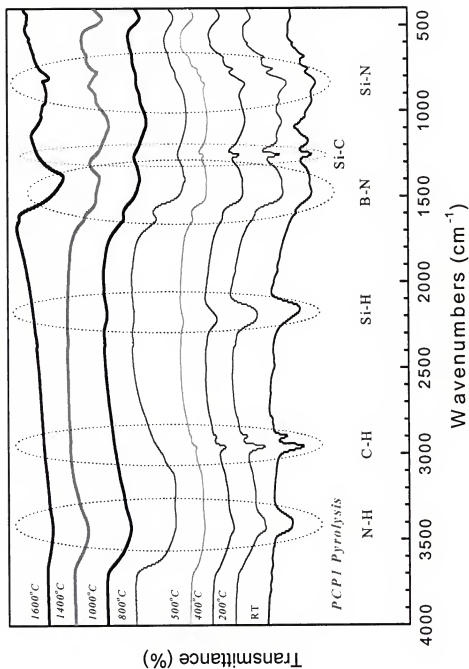


Figure 4-24. IR spectra of the preceramic polymer (PCPI) as a function of pyrolysis temperatures

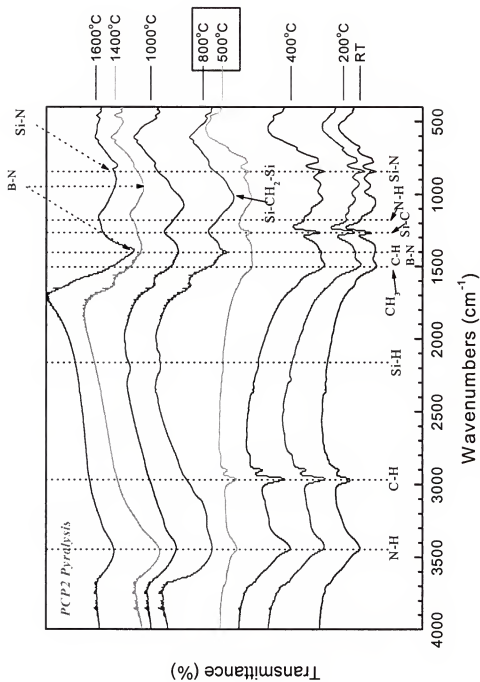


Figure 4-25. IR spectra of the preceramic polymer (PCP2) as a function of pyrolysis temperatures

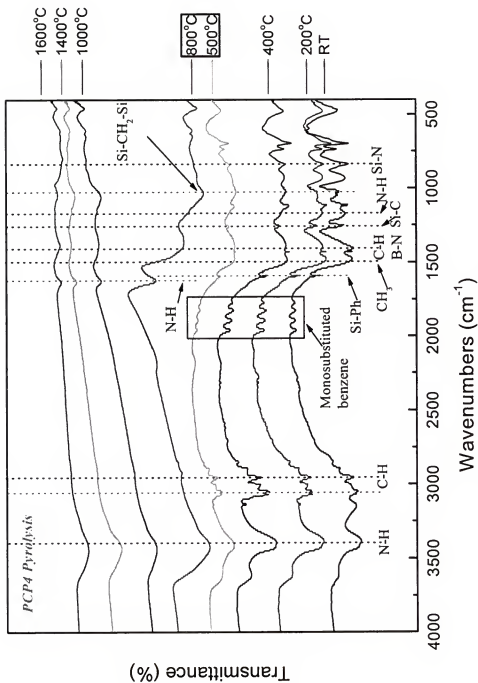


Figure 4-26. IR spectra of the preceramic polymer (PCP4) as a function of pyrolysis temperatures

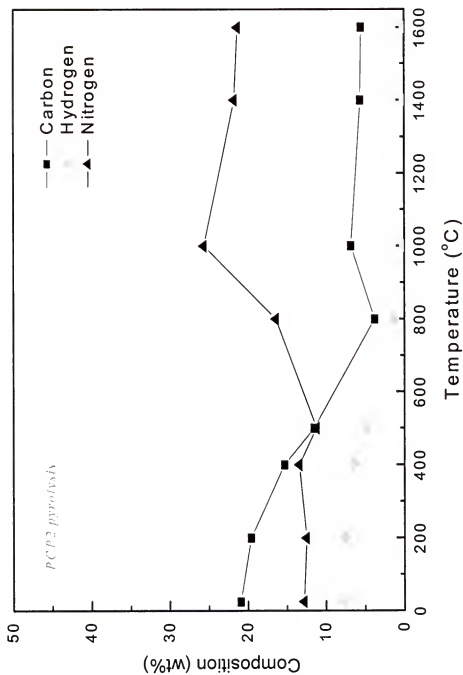


Figure 4-27. Compositional change of the preceramic polymer (PCP2) at different pyrolysis temperatures under argon atmosphere

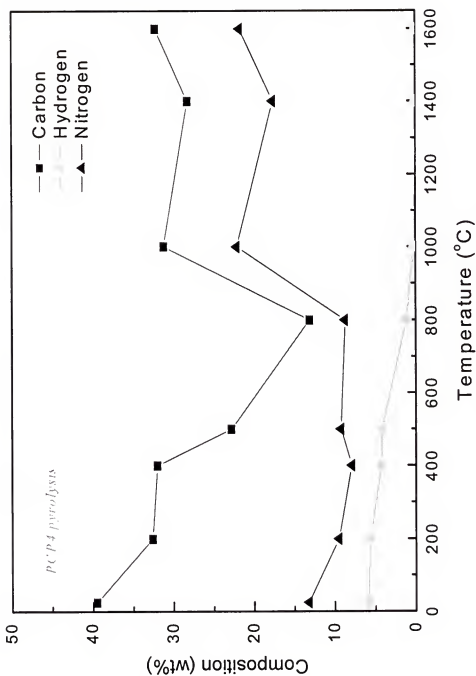


Figure 4-28. Compositional change of the preceramic polymer (PCP4) at different pyrolysis temperatures under argon atmosphere

Table 4-5. Weight loss of pyrolyzed polyborosilazanes at different temperatures and holding times

Temperature	PCP1	PCP2	PCP3	PCP4
500 °C for 1 h	26.5%	26.4%	24.0%	29.9%
800 °C for 1 h	27.3%	26.6%	37.8%	36.0%
1000 °C for 1 h	38.1%	37.0%	38.2%	41.8%
1600 °C for 1 h	48.7%	43.1%	43.5%	47.0%
1600 °C for 6 h	65.0%	56.9%	47.0%	58.0%
1600 °C for 12 h	70.0%	64.7%	54.0%	59.5%

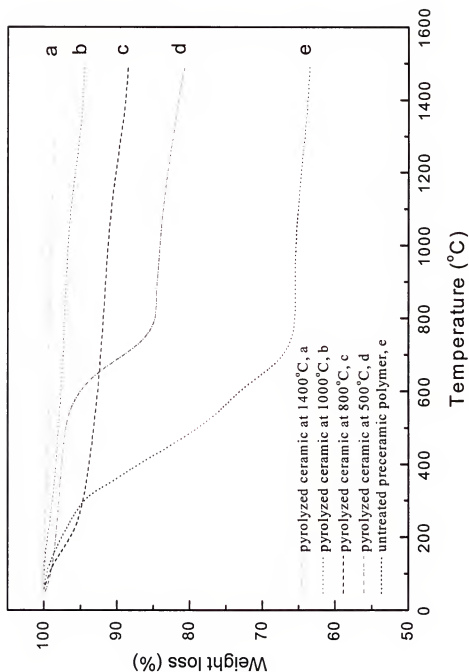


Figure 4-29. TGA curves of SiBCN ceramic pyrolyzed at 500, 800, 1000 and 1400°C

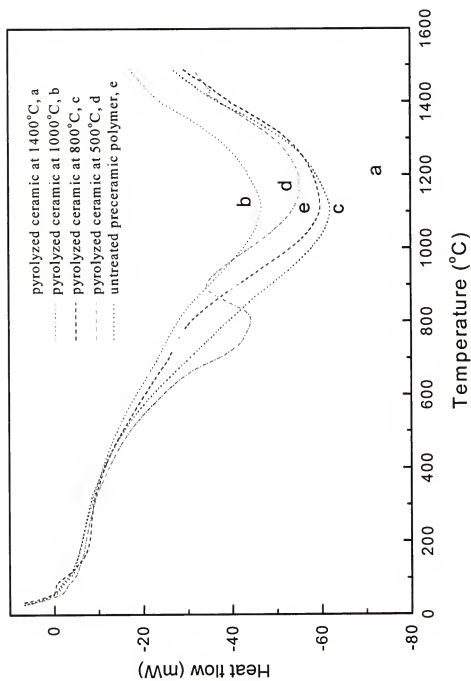


Figure 4-30. DSC curves of SiBCN ceramic pyrolyzed at 500, 800, 1000 and 1400 °C

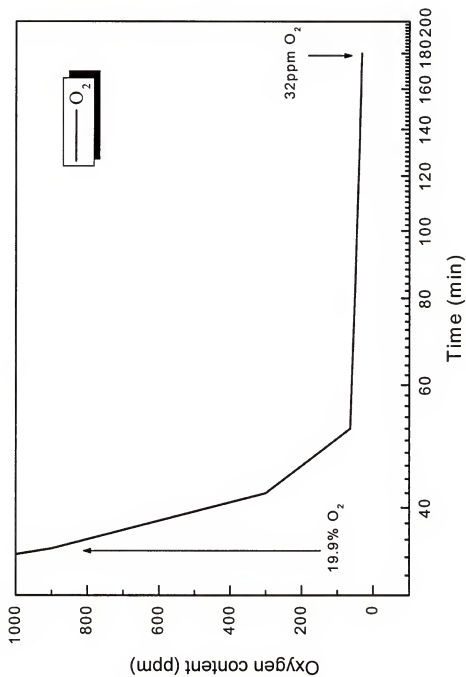


Figure 4-31. Change of oxygen content in the tube furnace with elapsed time

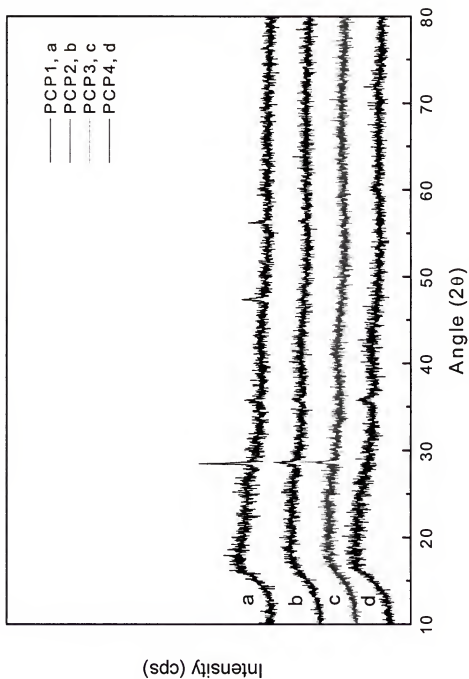


Figure 4-32. XRD peaks with different types of polyborosilazanes after pyrolysis at 1600 °C for 1 h under argon atmosphere

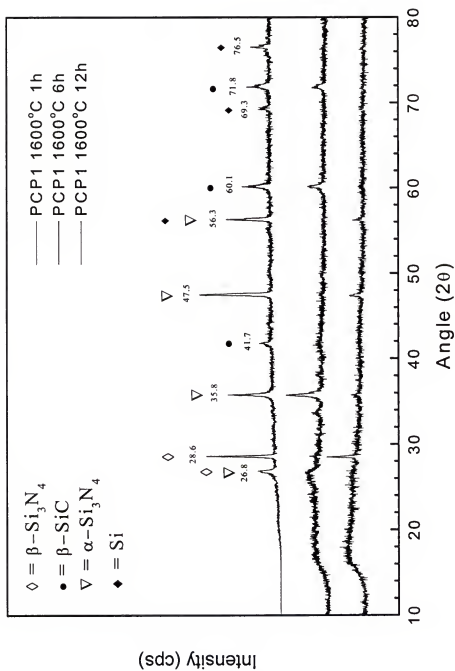


Figure 4-33. XRD peaks of polyborosilazane (PCP1) with different holding times during pyrolysis at 1600 °C under argon atmosphere

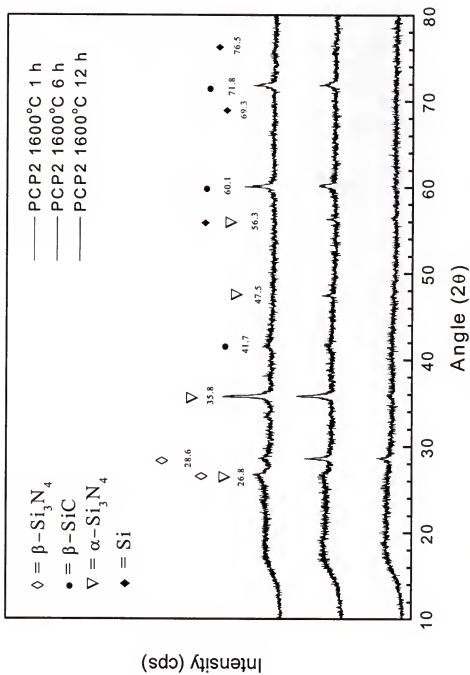


Figure 4-34. XRD peaks of polyborosilazane (PCP2) with different holding times during pyrolysis at 1600 °C under argon atmosphere

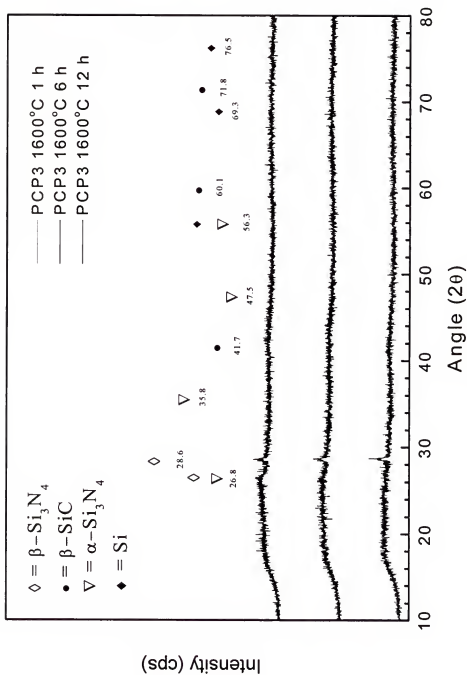


Figure 4-35. XRD peaks of polyborosilazane (PCP3) with different holding times during pyrolysis at 1600°C under argon atmosphere

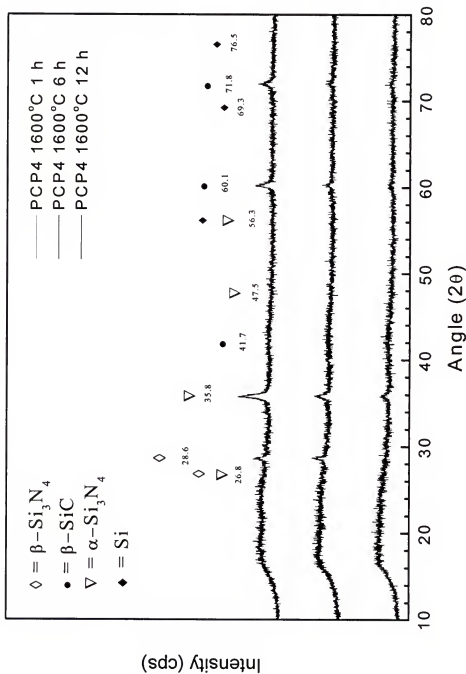


Figure 4-36. XRD peaks of polyborosilazane (PCP4) with different holding times during pyrolysis at 1600 °C under argon atmosphere

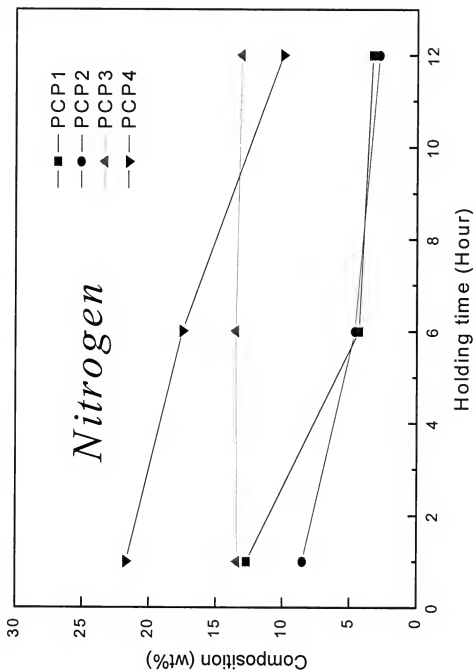


Figure 4-37. EA analysis of nitrogen content change in polyborosilazane with different holding times during pyrolysis at 1600°C under argon atmosphere

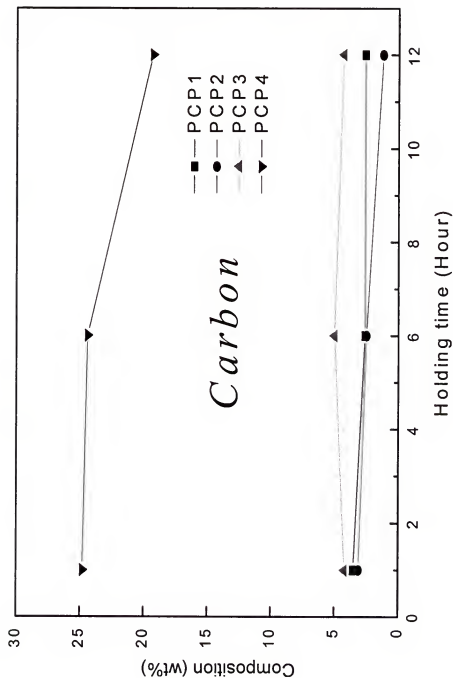


Figure 4-38. EA analysis of carbon content change in polyborosilazane with different holding times during pyrolysis at 1600 °C under argon atmosphere

Table 4-6. The ICP data of polyborosilazane preceramic polymer after autoclave test

Content	Data
Pellet weight	70 mg
Boron content of pellet	7.4 wt%
Boron content in blank water	0.76 ppm
Boron content in effluent	74.2 ppm
Boron in the Autoclave	1.1 ppm
Boron effluent from polymer pellet	200 ppm

CHAPTER 5 CONCLUSION

Hydrosilazane based polymers can be prepared by the reaction of disilazanes, such as hexamethyldisilazane (HMDZ), with trichlorosilane (HSiCl_3). Such polymers are useful, when fired at high temperatures, in the formation of silicon nitride and silicon nitride-containing ceramic materials. Organometallic polymers containing the elements of silicon, boron, carbon, nitrogen, and hydrogen, such as polyorganoborosilazanes, have been shown to have outstanding mechanical and chemical stabilities and to also be processable to form improved materials for high temperature applications. Boron is believed to provide enhanced thermal stability in SiCN-based materials. Such SiBCN organometallic polymers are precursors for ceramics including Si_3N_4 , SiC, and boron nitride-based SiBCN ceramics. On the basis of their high strength and oxidation resistance, these ceramics provide a unique combination of properties with respect to high-temperature applications compared to ceramics containing oxide.

In our study, a new synthesis method is established to prepare a SiBCN-based preceramic polymer derived from the reaction of hexamethyldisilazane, borontrichloride, and trichlorosilane at temperatures ranging from 127 °C to 300 °C. The method may allow polyborosilazane to be obtained in an affordable and simple manner without oxide compounds and undesirable salts. During the synthesis process, an additional step is not required to remove byproducts, which lead to significant chlorine content mixed with the polyborosilazane in the form of ammonium chloride crystals. The preceramic polymer can be directly formed exclusively by the described above reacting step. The chlorine

content of the preceramic polymer can be less than 200 ppm. Also, the crosslinking agents are not necessary. The hydrolysis of reaction material is prevented by using a special Schlenk-type benchtop technique.

The results obtained from various characterization techniques are in agreement with the postulated reaction mechanism and the structure of the preceramic polymer. The product is obtained from the reliable chemical reaction steps. All of the spectra in the IR and NMR correspond to the expected structures and bond formations. These characterization methods exhibit the distinct Si-N, B-N, and Si-C bands that indicate the quaternary ceramic component system. This could be the cause of the general SiBCN coordination detected by both IR and NMR. The relative abundance of the SiBCN preceramic polymer components is quantitatively determined by EA. The component of the preceramic polymer contains 29.4wt% Si, 7.4wt% B, 21.8wt% C, 10.6wt% N, and 7.4wt% H. The content of boron and hydrogen are enough to be used for the material related to nuclear reactor parts.

It has been verified in thermal analysis that there is a change in heat flow behavior at two temperature regions of 300 °C and 800 °C related to depolymerization of low carbon-connected molecules or hydrocarbons. The heat flow is involved in the molecular arrangement under crosslinking reaction of up to 1250 °C. The preceramic polymer starts to form a ceramic structure beyond this temperature. The preceramic polymer is substantially amorphous, as evidenced and defined by displaying no discernable X-ray diffraction peaks when X-ray diffraction is performed on the resulting preceramic polymer. The preceramic polymer retains the amorphous structure upon pyrolysis even when kept at 1600 °C for 1 h.

Two different types of the modification are presented by changing the potential reaction conditions and the starting monomers for a better quality. The chemical reaction is performed at a different maximum temperature from about 127 °C to 300 °C and at a different molar ratio from 1:1:4 to 1:1:6 (TCS:BTC:HMDZ) without a change in the initial monomers. It is evident that the temperature is not responsible for modifying the ceramic properties. However, the increase in the molar ratio offers a notable difference in the nature of the final product compared to the original prepared by the initial condition. The phase of the preceramic polymer turns into the gel state and the thermal stability of pyrolyzed preceramic polymer at 1600 °C for 12 h holding time have a considerable result according to XRD analysis. It indicates that the preceramic polymer is able to be used in the fiber fabrication and high temperature applications.

A modified method of forming SiBCN-based preceramic polymers comprises a reaction with a disilazane having the general formula $(\text{Me}_3\text{Si})_2\text{NH}$, RSiCl_3 where R is selected from the group consisting of methyl, ethyl and phenyl, and a boron halide including three halogens. The different compounds obtained from different monomers reveal that the results in XRD analysis contain a higher thermal resistance than observed in the preceramic polymer obtained previously. The use of ethyltrichlorosilane has an especially significant effect on the performance of the modified compound, which is similar to the result shown in the modified compound by increasing HMDZ content.

A SiBCN preceramic polymer or oligomer provides hydrothermal stability and at least 5 wt% hydrogen useful for burnable poison rod assemblies and spent fuel containers. For nuclear applications, significant hydrogen content is necessary to absorb and slow down neutrons, while hydrothermal stability is required for application

conditions. The possibility is assessed by the autoclave test. Under an extreme hydrothermal condition, the preceramic polymer holds its constituent without heavy loss. The boron effluent in the autoclave is as low as 200 ppm for 24 h. Therefore, this novel synthesis method and its products would provide the possibility to develop control of stoichiometry and to be used for hydrothermal applications.

The obtained polyborosilazane preceramic polymers in our study have been expected to provide the followings; 1) outstanding mechanical and chemical stability at very high temperatures enhancing product durability in the systems such as hybrid structural materials, advanced fiber composites, ceramic-matrix composites, hypersonic aircraft, space structural materials, micro/nano electromechanical systems and devices, 2) chemical makeup of polymer burns off poisonous waste more completely than current matrices reducing environmentally hazardous conditions, 3) streamlines processing of SiBCN-based polymer by eliminating unnecessary steps, 4) increased profit margins by reducing cost of processing in energy companies and launch equipment manufacturers.

Suggested directions include studies to continue the investigation of the preceramic polymers and to examine the effect on the different monomers' use for polymerization and the performance of the preceramic polymers in various applications. It would be of particular interest to examine the different chemical used the SiBCN system. First, a change of the number of chlorine functionality in the monomers would be provided. A total of six chlorines are available for substitution in BTC and TCS. HMDZs attacks chlorines at boron and silicon sites, as shown in Equation 4-1 of Chapter 4. The lower number of chlorine functionality in dimethyldichlorosilane (Me_2SiCl_2) would offer an opportunity for turning the rheological properties of the precursors. Moreover, the methyl

group will be connected to borontrichloride so that carbon has two covalent bonds instead of only one bond, which is the case when carbon is introduced through a methyl group. The product will also be compared to that obtained by change of pendant groups in trichlorosilane.

Second, a change of monomer with a different structure would be introduced in future studies. The increase in carbon content would provide the thermal durability of the resulting SiBCN ceramics, as can be seen from the thermal stability of SiBN compared to SiBCN. The modified preceramic polymers showed large weight loss during pyrolysis at 200 °C to 800 °C. Their loss is relieved by an introduction of carbon between silicons. The increase in carbon content by way of changing the original TCS (HSiCl_3) or ETCS ($\text{CH}_3\text{CH}_2\text{SiCl}_3$) for trichlorotrimethylsilylethylsilane ($\text{Me}_3\text{SiCH}_2\text{CH}_2\text{SiCl}_3$) can be attained. It is interesting to note that the side group (CH_3CH_2-) attached to silicon is easy to decompose during pyrolysis or high temperature use. On the contrary, the ethyl group ($-\text{CH}_2\text{CH}_2-$) between two silicon atoms can maintain its bond without decomposition during pyrolysis or high temperature use. It is recommended that the evolution mechanism of the structure of the modified products at elevated temperature should be clearly identified by spectroscopic analysis such as MAS-NMR.

Finally, it can also be of great interest to investigate the effect of increasing borontrichloride (BTC) content on the hydrothermal performance of the preceramic polymer in several nuclear field applications. The chemical composition of the preceramic polymer can be tailored to achieve the desired amount of element present. The enrichment of boron in an amorphous preceramic polymer plays a crucial role as the surrounding material in a nuclear reactor in that it absorbs neutrons at a faster rate. Boron

has a structural hindrance for chain arrangement to form an ordered crystalline region.

Several research groups reveal that minimum boron content is required to protect the ceramic materials from decomposition, even though the appropriate boron content of the polyborosilazane preceramic polymers exists in the upper limit. In future research, the boron content could be doubled (2:1:4) or tripled (3:1:4) beyond the levels of our study and eventually compared with the product obtained from the monomer feed content 1:1:4.

APPENDIX A

ABBREVIATION AND CHEMICAL FORMULAE

Abbreviation	Full name
PCP	Preceramic polymer
TCS	Trichlorosilane
BTC	Borontrichloride
HMDZ	Hexamethyldisilazane
BPRA	Burnable Poison Rod Assembly
SFC	Spend Fuel Container
PWR	Pressurized Water Reactor
CMC	Composite Matrix Ceramic
CVC	Chemical Vapor Curing
CVD	Chemical Vapor Deposition
CLD	Chemical Liquid Deposition
HMPA	Hexamethylphosphortriamide
HPZ	Hydridopolysilazane
PDMS	Poly(dimethylsilane)
PS	Polysilane
PSCS	Polysilacarbosilane
PSP	Polysilapropylene
PSSZ	Polysilasilazane
PSZ	Polysilazane
PCS	Polycarbosilane
PCSZ	Polycarbosilazane
PBS-Me	N-methylpolyborosilazane
TADB	(Trichlorosilylamino)dichloroborane
TABB	Tris(dimethylamino)silylamino-bis(dimethylamino)-borane
TMS	Trimethylsilyl or Tetramethylsilane
THF	Tetrahydrofuran
MADB	(Methyldichlorosilylamino)-dichloroborane
DADB	(Dimethylchlorosilylamino)-dichloroborane
TSDM	Trichlorosilyl-dichloroboryl-methane
DSDM	Dichloro(methyl)silyl-dichloroboryl-methane
TSMB	B,B',B''-trichlorosilylmethyl-borazine
DSMB	B,B',B''-dichloro(methyl)silyl-methyl-borazine
DMTA	Dichloroboryl-methyl-trichlorosilyl-amine
TSDE	1-(dichloroboryl)-1(trichlorosilyl)-ethane
FT-IR	Fourier Transform Infrared
DRIFT	Diffuse Reflectance Infrared Fourier Transformation
ATR	Attenuated Total Reflectance

MFC	Monomer Feed Content or Mass Flow Controller
MAS-NMR	Magic Angle Spinning Nuclear Magnetic Spectroscopy
CP	Cross Polarization
EA	Elemental Analysis
XRD	X-ray Diffraction
AA (or AAS)	Atomic Absorption Spectroscopy
EDS	Energy Dispersive (x-ray) Spectroscopy
TA	Thermal Analysis
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
ICP	Inductively Coupled Plasma
T _g	Glass Transition Temperature
T _c	Crystallization Temperature
T _m	Melting Temperature

Chemical formulae	Chemical name
HSiCl ₃	Trichlorosilane
CH ₃ SiCl ₃	Methyltrichlorosilane
C ₂ H ₅ SiCl ₃	Ethyltrichlorosilane
C ₆ H ₅ SiCl ₃	Phenyltrichlorosilane
(CH ₃) ₃ SiCl ₂	Dimethyldichlorosilane
(CH ₃) ₃ SiCH ₂ CH ₂ SiCl ₃	Trichlorotrimethylsilylethylsilane
(CH ₃) ₃ SiNHSi(CH ₃) ₃	Hexamethyldisilazane
C ₆ H ₁₄	Hexane
NH ₃	Ammonia
CH ₃ NH ₂	Methylamine
(CH ₃) ₃ SiNH-	Trimethylsilylamino
NH ₄ Cl	Ammonium chloride
(CH ₃) ₄ Si	Tetramethylsilane
SiC	Silicon carbide
Si ₃ N ₄	Silicon nitride
B ₄ C	Boron carbide
BN	Boron nitride
Al ₂ O ₃	Alumina

APPENDIX B

POLYBOROSILAZANE SOLUTION FORMULATION

The formulations for chemical solutions used in the synthesis of polyborosilazanes described in Chapter 4 are outlined briefly. The final products were white and bulky solids except PCP1116 in gel phase.

PCP1

- Molar ratio = 0.03:0.03:0.12mol = 1:1:4
- 4.2g trichlorosilane (98%)
- 22.2g borontrichloride (100%)
- 20.0g hexamethyldisilazane (97%)
- 300rpm stirring
- Final reaction temperature 200 °C
- No filtering and vacuum

PCP1116

- Molar ratio = 0.02:0.02:0.12mol = 1:1:6
- 2.8g trichlorosilane (98%)
- 14.8g borontrichloride (100%)
- 20.0g hexamethyldisilazane (97%)
- 300rpm stirring
- Final reaction temperature 300 °C
- No filtering but vacuum applied

PCP2

- Molar ratio = 0.025:0.025:0.10mol = 1:1:4
- 3.8g methyltrichlorosilane (97%)
- 18.3g borontrichloride (100%)
- 16.5g hexamethyldisilazane (97%)
- 300rpm stirring
- Final reaction temperature 200 °C
- No filtering and vacuum

PCP3

- Molar ratio = 0.03:0.03:0.12mol = 1:1:4
- 5.0g ethyltrichlorosilane (99%)
- 22.2g borontrichloride (100%)
- 20.0g hexamethyldisilazane (97%)
- 300rpm stirring
- Final reaction temperature 200 °C
- No filtering and no vacuum

PCP4

- Molar ratio = 0.03:0.03:0.12mol = 1:1:4
- 6.7g trichlorosilane (95%)
- 22.2g borontrichloride (100%)
- 20.0g hexamethyldisilazane (97%)
- 300rpm stirring
- Final reaction temperature 200 °C
- No filtering and no vacuum

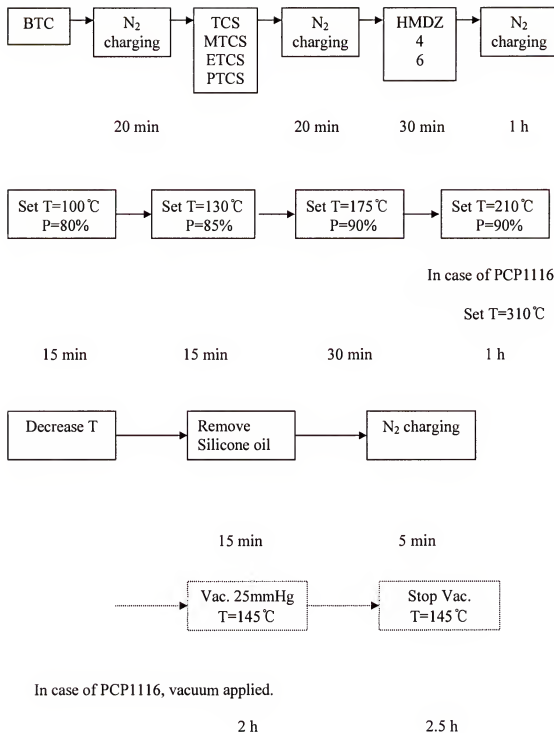


Figure B-1. Flow chart of polymerization

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BIOGRAPHICAL SKETCH

Jongsang Lee was born in Daejeon, South Korea. He received his bachelor's and master's degrees in polymer science and engineering from Chungnam National University, South Korea. He completed his Ph.D. at the University of Florida, in the Department of Materials Science and Engineering. Jongsang Lee previously conducted research at the Division of Material Research in the Korea Institute of Science and Technology's Center for Polymer Hybrids. At Taekwang Institute of Technology he was a field engineer for the Division of Carbon Fiber Research in Carbon Fiber and Composite Materials Lab and Carbon Fiber Plant, and a senior researcher in the Division of Polymer Research in the Synthetic Fiber Lab.

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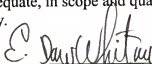
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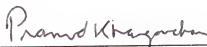


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